SOME ASPECTS OF THE LUMINESCENCE OF SOLIDS

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BY

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PREFACE

This book is based on experimental work carried out in the physical laboratory of the N.V. Philips Gloeilampenfabrieken, Eindhoven, Netherlands, during the last five years. It does not pretend to give a complete presentation of the present knowledge regarding the phenomenon of luminescence in solids, nor does it give a general survey. It contains some hitherto unpublished experimental results together with theoretical considerations of certain aspects of this field of science.

In the first chapter a brief consideration is given of the energy levels in pure and perturbed crystals. Starting from this point, an attempt is made to develop a general picture, capable of covering all possible luminescent effects. The emissions of activated luminophors reported in the literature have been tabulated according to the activator and it has been tried to classify them according to this scheme. Some subjects of particular importance like excitation, energy transport and sensitization have also been discussed.

In four further chapters new experimental results are reported concerning some particular luminescent systems, viz., tungstates, molybdates and luminophors activated by manganese, titanium and uranium. With manganese special attention has been paid to the valency in which it acts as an activator, leading to the discovery of the activating properties of tetravalent manganese besides those of divalent manganese already known.

In the sixth and final chapter the influence of the temperature on the efficiency of luminescence has been considered. It contains a survey of experimental data to be found in the literature, together with new results obtained by the author. Furthermore the phenomenon has been treated theoretically, and finally, theory and experiment have been confronted and are found to agree reasonably.

The author is greatly indebted to Dr E. J. W. VERWEY, Prof. Dr H. B. G. CASIMIR and Ir H. RINIA, directors of this laboratory, for permitting him to publish this book.

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I. A GENERAL CONSIDERATION OF THE PHENOMENA OF LUMINESCENCE

1. INTRODUCTION

When a system absorbs energy in some form or other, it may be partly re-emitted as radiation. This phenomenon is called luminescence. Luminescence may occur in solids (crystals or glasses) as well as in liquids or gases. In this book only the luminescence in crystalline solids will be discussed.

The mechanism of the process by which luminescence is generated varies from comparatively simple to rather intricate ones. In the simplest cases the process consists of two immediately connected parts, the absorption of energy and the emission of a corresponding radiation (resonance luminescence). In the more intricate cases additional processes occur in between, such as the transfer of energy or a partial dissipation of the excitation energy, while also parallel processes may occur in competition with those leading to luminescence, in which the excitation energy is totally dissipated.

The mechanism of the processes may be advantageously described with the aid of energy schemes showing the different energy states in which the system can occur in consequence of different electronic configurations. The lowest energy state is the state in which the system exists normally; it is called the ground state. The higher states are called excited states.

When crystals are excited by the absorption of light, it may be assumed that each quantum of light excites one electron. According to quantum theory the quantum $h\nu$ must be exactly identical with the energy difference ΔE between the ground state and the particular excited state, and the frequency ν of the absorbed light is accordingly determined by the relation

$$\nu = \frac{\Delta E}{h}$$

in which h is PLANCK's fundamental constant. The frequency of an emitted radiation is connected with the energy difference between the excited state and the ground state by exactly the same relation. In this respect the emission is perfectly equivalent with the absorption.

For excitation by corpuscular rays (α, β, or electrons liberated in the solid by X-rays) the situation is a little more complicated. Each corpuscle penetrating into the solid with a large kinetic energy gradually looses energy in collisions with the electrons of the crystal and thus causes the excitation of a number of these, so called secondary electrons. The nature of the luminescence is the same for both kinds of excitations, the frequency of the radiation being determined solely by the energy states of the system.

For the sake of simplicity we shall only discuss the luminescence excited by light (photo-luminescence). We shall examine the energy states both of ideal pure crystals and of perturbed crystals containing either lattice defects or foreign ions; we shall consider the possible optical transitions; and finally we shall discuss some further important phenomena related to luminescence.

In the next section a survey of the different energy schemes which are in use are given together with a rather formal discussion of their applicability and the methods to derive them. In the sections following it (3) the same considerations re-appear in a more concrete form, the different cases being treated more in detail.

2. ENERGY SCHEMES AND THEIR DERIVATION.

There are two schemes which are commonly used for the description of the energy states in which a crystal may occur as a consequence of its electronic configuration. In the first type of scheme the energy levels of the electronic configuration of the crystal as a whole are indicated. The energy of a state can be defined as the energy liberated in forming the lattice in this state from the atoms under standard conditions. For sodium chloride, for instance, the energy per mol

can be defined with respect to that of one mol of sodium metal and half a mol of chlorine vapour of one atmosphere. In principle these energy values can be determined exactly by experiment as well as by means of quantum mechanics.

For many purposes, however, a second scheme is more elucidating. This scheme originates in an approximate treatment of the electronic configuration, in which it is supposed that each electron can occupy one of a number of available orbits in accordance with the exclusion principle. An orbit may be such that an electron, occupying it, is localized on a special atom (atomic orbit, HEITLER–LONDON approximation), or it may extend through the whole crystal (crystal orbits, BLOCH approximation). In this picture the type of orbit which provides the best starting point for an approximate treatment depends on the type of the crystal and the orbits in which we are interested. In cases where the electrons are practically free, such as the conduction electrons in metals and probably the electrons occurring in the higher excited states of insulators, crystal orbits are preferably used. The electrons of the inner shells of atoms in all solids can be successfully regarded as occupying atomic orbits and also for many problems concerning the ground state and the lower excited states of the valency electrons in insulators, these orbits can be used. Those problems in which we are especially interested, namely the problems which we meet in the study of optical processes, fall into this category [1].

In the orbital picture the energy of the levels of individual orbits can be defined by the energy required to take one electron out of an orbit and to remove it to an infinite distance. If the crystal is in the ground state a number of levels is occupied with electrons, different levels indicating that the electrons are bound with various strengths. Excitation of the crystal may be described as the excitation of an electron and accordingly in the orbital level scheme of an excited crystal electrons are present in levels corresponding to excited orbits which are normally unoccupied. The energy of such excited

[1] Compare J. C. SLATER, *Trans. Far. Soc.*, **34** (1938) 828.

levels can be defined in the same way as that of the occupied levels, namely by the energy which is required to bring an electron occupying one of these orbits, from these orbits to infinity.

When working with atomic orbits, care must be taken of the fact that the energy of an excited orbit is dependent on its position in space with respect to the orbit from which an electron has been raised in the excitation process: The electron in its new orbit and the hole in the orbit from which the electron has been taken interact electrostatically. We meet this situation in the atomic orbital description of the excited states of the valency electrons in an ionic crystal which correspond to electronic transfer between ions at various distances.

So far we have neglected the fact that in a stationary state an electron cannot be considered as belonging to a particular ion but moves continually from an atomic orbit in one ion to equivalent orbits in other ions. We call this quantum mechanical effect "resonance" or "place exchange" [1]. The atomic orbit picture does not account for this effect, though it may provide a starting point for a further approximation which includes the place exchange to a certain extent. The place exchange is however essentially accounted for in the crystal orbit picture. The description of the electronic states of a crystal by means of crystal orbits leads to an energy scheme containing energy bands instead of sharp levels. Yet also in this case the description is not perfectly satisfactory, as we meet with the following complication. In the ground state the occupied crystal orbits have energy values which can be determined in the way described above. In addition there are several excited states of the crystal which can satisfactorily be described with crystal orbits, namely those states in which

[1] The effect should not be confused with the quantum mechanical exchange effect. The latter follows from the fact that the crystal wave function is anti-symmetrical in the electrons and therefore occurs solely in many-electron problems. The place exchange however must already be taken into account if we are dealing with one electron for which a number of equivalent positions are available, e.g., an electron in a periodic crystal field.

— speaking in the atomic orbital language — electrons and holes practically do not interact. Excitation to these states can reasonally be described as the lifting of an electron from an occupied level into an unoccupied excited orbit. Excited states of the crystal in which electrons and holes do interact mutually (excitons, cf. section 3.2) can however not be handled with the aid of crystal orbits. At most the crystal orbits may be used as a starting point for a further approximation in which it can no longer be said that each electron occupies a certain orbit [1].

Hence a complete and at the same time correct electronic scheme of the energy states of a crystal cannot be obtained with either of the two approximations which we have at our disposal at the moment.

In the next sections we shall consider the atomic- and crystal orbit approximations a little more in detail, and we shall try to obtain a complete scheme of the energy states of a crystal. The following procedure will be used. First we shall discuss the energy levels of the electronic orbits with the atomic orbit method as a starting point. With the aid of these levels we construct a picture of the energy states of the crystal as a whole. After this we shall discuss the effect of electronic place exchange on these states. Also we shall discuss the crystal orbit approximation in the case of place exchange and its limitations with respect to the description of certain excited states.

3. THE LEVELS OF PURE IONIC CRYSTALS

3.1 *The atomic orbit approximation*

Let us choose as a model for an ionic crystal, a crystal built up of univalent ions A^+ and B^- in a state of complete rest. The energy states of this crystal may be derived by starting from a sort of expanded crystal lattice, in which the ions A^+ and B^- are already placed according to the pattern of the real lattice, but in which the mutual distances are so

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[1] G. H. WANNIER, *Phys. Rev.*, **52** (1937) 191.

large that there are no interactions between the ions [1]. Obviously the occupied electronic orbits in this expanded crystal are identical with those in the free ions, while the energy values are completely determined by the dissociation energy and the electronic affinity of the constituent ions. Several excitation processes are possible in the crystal, of which six important examples are schematically given by:

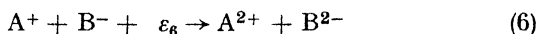
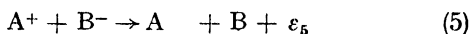
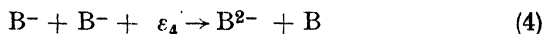
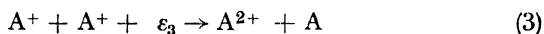
$$A^+ + \varepsilon_1 \rightarrow A^{+*} \tag{1}$$

$$B^- + \varepsilon_2 \rightarrow B^{-*} \tag{2}$$

$$A^+ + A^+ + \varepsilon_3 \rightarrow A^{2+} + A \tag{3}$$

$$B^- + B^- + \varepsilon_4 \rightarrow B^{2-} + B \tag{4}$$

$$A^+ + B^- \rightarrow A + B + \varepsilon_5 \tag{5}$$

$$A^+ + B^- + \varepsilon_6 \rightarrow A^{2+} + B^{2-} \tag{6}$$

The quantities $\varepsilon_1 \ldots \varepsilon_6$ stand for the change of energy accompanying the process, while the asterisks denote excited states of ions. Two types of processes may be distinguished. An electron is either excited within its own ion, giving rise to excited ions A^{+*} or B^{-*} [2] (processes (1) and (2)), or it is brought from one ion to another one (processes 3—6). The latter processes are called *transfer* transitions [3].

In Fig. 1*a* we give an energy scheme of the electronic orbits in the expanded crystal. Orbits occupied in the ground state are drawn with heavy lines, while excited orbits which are normally unoccupied, are drawn in fine lines. The interpretation of this energy scheme calls for a certain amount of caution. The energies of the orbits of the valency electrons of A^+ and B^- are defined in the conventional way and are determined by the dissociation energies. In the figure the energy values have

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[1] J. C. SLATER–W. SHOCKLEY, *Phys. Rev.*, **50** (1936) 705. F. SEITZ, *Modern Theory of Solids* (1940) p. 448.

[2] If the negative ions have no definite excite state(s) below the ionisation limit, the B^{-*} level has to be replaced by the ionisation continuum of these ions. This is the case for most simple negative ions, such as the chlorine ion.

[3] The term *transfer-* was introduced by E. RABINOWITCH, *Rev. Modern. Phys.*, **14** (1942) 112 in connection with spectra due to electronic transitions between different atoms, instead of the much less suggestive term *affinity spectra* used before.
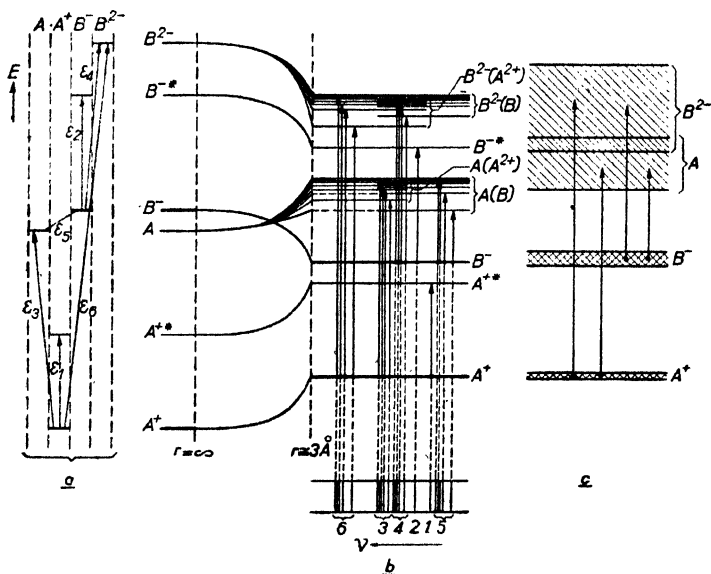
Fig. 1.

a. Orbital energy states of separate ions, and electronic transitions involving these states.

b. Change in the position of orbital levels upon condensation of the separate ions to a crystal (no electronic place exchange). The absorption spectrum of the condensed crystal is given underneath.

c. The energy band picture of the crystal.

been plotted in such a way that an increase of dissociation energy causes a lowering of the levels. It must be remembered that the levels A^+ and B^- are highly degenerate. Each individual ion gives rise to an orbit and therefore there are as many orbits with identical energy as there are identical ions. The energy of the excited orbits A^{+*} and B^{-*} are defined in the same way as the normal orbits, but it must be kept in mind that the occupation of this orbit only has meaning if the ground state orbit of the corresponding A^+ ion is empty.

The excitation process (1) can be described by the lifting of an electron from the A^+ into the A^{+*} level in one of the A^+ ions; process (2) is analogous. In order to describe the

four other excitation processes mentioned, we have to introduce some additional orbits into our picture, namely the orbits of an outer electron in the A atom and in the B^{2-} ion which are formed in these excitation processes. The energies of these orbits are again defined by the ionization energies of the A atoms and the B^{2-} ions [1].

Process number 3 can be indicated by the lifting of an electron from level A^+ into level A. The energy necessary for this process is, by our convention, equal to the energy required to strip off an electron from an A^+ ion minus the energy required to ionize an A atom. Process number 5 can be indicated by the transfer of an electron from a B^- into an A level. It is seen that in this process energy is liberated, corresponding to the fact that in the infinitely expanded lattice the lowest energy state does not correspond to an ionic lattice, but to a configuration of neutral atoms [2].

Now suppose that the ions of the expanded crystal are gradually brought together. We have to consider what happens to the energy levels of the orbits and to the description of the excitation or transfer processes. In order to simplify the discussion we assume that the mutual interaction is sufficiently accounted for by an electrostatic interaction of the ions; a further approximation would have to include polarisation effects, VAN DER WAALS attraction, and repulsion effects [3]. Since a positive ion is preferentially surrounded by negative ions the atomic orbits of a positive ion (A^+ and A^{+*} levels) are raised in our figure by an amount Me^2/r, where r is the shortest distance between a positive and a negative ion and M is a factor dependent on the configuration of the lattice. M is

[1] In many cases a B^{2-} ion will not be stable. Then the B^{2-} level must be replaced by a continuum from zero energy upwards.

[2] There are a few exceptions, as CsF, for instance, in which coexisting Cs^+ and F^- ions are stable in the expanded configuration.

[3] J. H. DE BOER, *Z. f. phys. Chem.*, (B) **18** (1932) 49.
W. KLEMM, *Z. f. Phys.*, **82** (1933) 529.
A. VON HIPPEL, *Z. f. Phys.*, **101** (1936) 680.
N. F. MOTT–M. J. LITTLETON, *Trans. Far. Soc.*, **34** (1938) 485.
N. F. MOTT–R. W. GURNEY, *Electronic Processes in Ionic Crystals* (1940) p. 58, 95.

closely related to the MADELUNG constant which determines that part of the lattice energy which is caused by the COULOMB forces [1]. Analogously the levels B^- and B^{-*} are both lowered by the same amount. Thus in this approximation the excitation energy of the processes (1) and (2) is not altered by the gradual contraction of the ionic lattice. The situation is more complicated, however for the states A and B^{2-} which are reached in a transfer process. Let us consider first the process (3) in which an electron is transferred from an A^+ ion to neutralize another A^+ ion, leaving an A^{2+} ion behind. The energy of the A orbit which the electron occupies after the transition is defined in the same way as the energy of the ground levels, viz., as the energy required for the removal of an electron out of the orbit to infinity. Since the ion A^+ and the atom A formed are both placed at positive lattice positions, the energy of the levels A and A^+ between which the electron jumps in the transition are changed by the lattice contraction in the same direction, namely they rise both. If there is no interaction between the atom A and the A^{2+} ion which is created in the transition, i.e., if their mutual distance R is large, the amount of the change is also the same, being Me^2/r for both. If the distance R is smaller, however, the energy of the excited state A is lower by an amount e^2/R due to electrostatic interaction of the electron at the A atom with the A^{2+} ion. This can easily be seen, since the A^{2+} ion behaves like an extra positive charge. In this way a series of excited levels A (A^{2+}) is obtained which have risen by an amount $(Me^2/r - e^2/R)$ with respect to the levels of the expanded lattice, and of which the lowest level corresponds to a transition to a neighbouring ion. It can be shown in the same way that the process (4) in which an electron is transferred from a B^- ion to another B^- ion, forming a B^{2-} ion, gives rise to a similar series of B^{2-} (B) levels. The only difference with

[1] It can easily be shown that for a crystal built up of $n_1, n_2, \ldots . n_i$ ions of a valency $v_1, v_2, \ldots . v_i$, the constants $M_{1, 2 \ldots i}$ determining the energy due to the COULOMB forces of the surroundings at the different lattice points are connected with the MADELUNG constant A by the relation $A = \frac{1}{2} \sum_i n_i v_i M_i$. Therefore only for crystals consisting of monovalent ions is M identical with A.

process (3) is that the levels B^- and B^{2-} between which the transition occurs, now fall instead of rise as a consequence of the contraction of the lattice.

For the processes (5) and (6) in which electrons are transferred between ions of opposite sign, namely from A^+ to B^- and from B^- to A^+, the influence of the interaction between the excited electron and the ion formed in the transfer process is similar to that which has just been discussed for the transitions between ions of corresponding sign. Two series of excited levels A (B) and B^{2-} (A^{2+}) are obtained, in which the separation of the sub-levels is again given by e^2/R. The series of excited levels A (B) and A (A^{2+}) have a common series limit towards which the sub-levels crowd together. They differ in their lower members, however, due to the fact that the distances R from one A position to other A positions are different from those between an A position and B positions. The same holds for the series B^{2-} (A^{2+}) and B^{2-} (B). A marked difference between the excitation processes in which electrons are transferred between ions of corresponding sign (3, 4) and between ions of opposite sign (5, 6), consists in the energetic position of the series of excited levels with respect to the ground levels. While in the first case excited levels and ground levels are both changed in the same direction due to the contraction of the lattice, in the latter case the direction of this change is opposite; levels of ions at positive positions rising, of ions at negative positions falling. As a consequence the transfer transitions of process (6) cost $(2Me^2/r + e^2/R)$ less energy in the contracted lattice than in the expanded lattice, while the transitions of process (5) cost $(2Me^2/r - e^2/R)$ more. In fact for a normal ionic crystal this change is so large that the transitions of (5) which yield energy in the expanded configuration, cost energy in the contracted lattice; the levels A and B^- cross [1].

[1] This is a necessary consequence of the fact that the crystal we are considering is stably built up of oppositely charged ions of the valency assumed. If the levels A and B^- would not cross, this would indicate that our starting point had been incorrect, the actual crystal either consisting of ions of a different valency, or being built up of more or less covalently bound atoms.

In Fig. 1*b* the effects of the lattice contraction on the various levels have been indicated. From this picture the excitation processes so far considered can be read. As an example we may consider all the excitation processes in which an electron is raised from an A^+ ion. The process involving the least energy is the excitation of the A^+ ion itself. The next is the transfer to the nearest neighbouring A^+ ion, i.e., to the lowest of the series of A levels. Next there is a large number of transfer processes to A^+ ions which are at larger distances. Finally we have the possibility of transfer to B^- ions in the neighbourhood or at larger distances. In exactly the same way the possible excitation processes of a valency electron of a B^- ion may be derived. From these considerations, based upon the orbital picture, we can automatically obtain the excited states of the crystal as a whole. The energy scheme describing the states of the entire crystal is shown in Fig. 2*a*. It contains one single ground level and several excited levels. Each excited level corresponds to a particular excitation process in the orbital picture, the separation between the excited levels and the ground level being identical with the energy differences marked by arrows in the orbital scheme (Fig. 1*b*). The different excited energy levels of the crystal as a whole are still far more degenerate than N, the degeneracy of the orbital levels. The degree of degeneration is equal to the product of the number of equivalent ions (N) in the crystal, from which, speaking in the orbital language, the excited or transferred electron may be supposed to have been lifted, with the number of orbits to which the electron can be transferred situated at the same distance from the ion of origin. It must be emphasized that the approximation used until now, neglects the effect of electronic place exchange upon the various states of the crystal. This effect will be considered in the next section.

3.2 *The effect of electronic place exchange*

In the preceding section we have obtained a scheme containing the ground state and the excided states of the crystal as a whole. It was derived on the basis of atomic orbits and

each excited state was found to be highly degenerate. The theory predicts that this degeneracy will vanish in a finer quantum mechanical approximation, namely when the so called "place exchange" effects are taken into account. Each degenerate excited energy level of the crystal as a whole
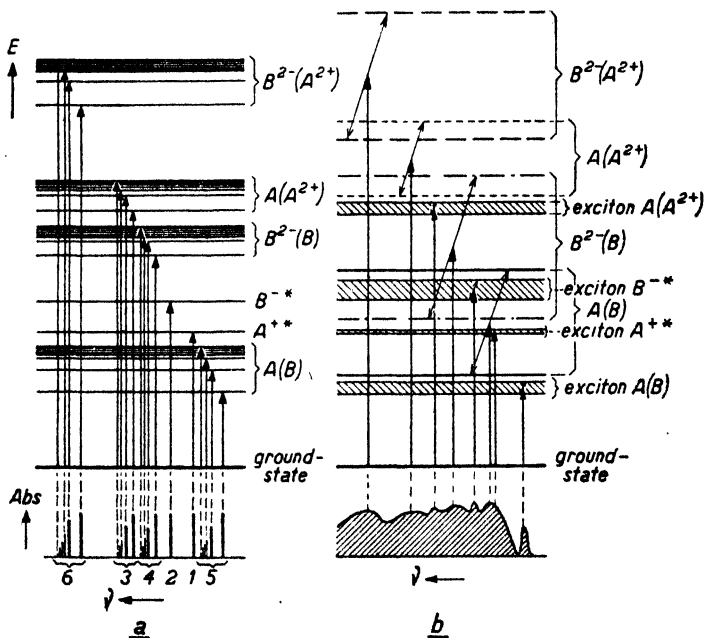
Fig. 2. Energy states of a crystal as a whole (*a*) without or (*b*) with allowance for electronic place exchange, together with the possible excitation transitions and the corresponding absorption spectra.

will broaden into a band of levels. We shall try to explain this by the following consideration. Let us take the excited state of the crystal, called A^{+*} in Fig. 2*a*, as an example. This state of the crystal arises in our orbital picture from the excitation of one special A^{+} ion and the state is degenerate, because there are so many ions which may be excited. According to quantum mechanics in the actual energy states of the crystal, the state

of being excited is not restricted to one special atom, but moves from one A^+ ion to another through the lattice. Such a moving excited state of an atom or ion was called an exciton by FRENKEL[1]. The exciton may have different velocities and the different kinetic energies associated with this movement cause the different values of energy of the individual levels in the band of energy states of the crystal as a whole (exciton band A^{+*}, Fig. 2*b*).

In the atomic orbital picture it is obvious that for the motion of an exciton an uninterrupted interchange of electrons between A^+ ions must take place. The electron in the excited A^{+*} orbit of a certain ion must jump to the excited orbit of a neighbouring A^+ ion, while at the same time the electron in the A^+ orbit of this ion jumps into the A^+ orbit of the first ion. The latter process is commonly described as the moving of a "hole" in the A^+ level from the first to the second ion. The probability for exchange is the greater the more the wave functions of the orbits involved overlap, and the resulting broadening of the excited levels of the crystal as a whole increases with it. Compare for instance the broadening of the B^{-*} level with that of the A^{+*} level in Fig. 2*b*.

An analogous argument holds for the levels of the crystal as a whole which originate from transfer processes, for instance, process number 5. Here also the broadening is caused by the fact that both the transferred electron and the hole it left behind may travel through the lattice. For cases where the distance of transfer is small (transfer processes to neighbouring ions) the distance between electron and hole remains constant during the migration through the crystal. In these cases a separate excitation band ("exciton band") with this origin may be distinguished in a scheme of crystal energy states. For the higher transfer levels, however, the broadening causes an intermingling of bands. Here it gradually becomes inadequate to speak of an electron bound to its hole, and a better approximation is to consider an electron and a hole moving independently through the lattice, each with its own velocity. A typical feature of the latter states is the possibility of elec-

[1] J. FRENKEL, *Phys. Z. Sowjet Union*, **9** (1936) 158.

trical conductivity by the electrons and also by the "holes", which behave as mobile positive charges. On the other hand in the states where the negative electron and the positive hole are strongly bound together, an applied electric field has no effect.

In Fig. 2*b* we have indicated four exciton bands above the ground state of the crystal, two arising from characteristic excitation processes (A^{+*} and B^{-*}), the other ones from the cheapest transitions of the transfer processes (3) and (5) in the orbital picture [A (B) and A (A^{2+})]. The formal distinction we have maintained so far between these two kinds of exciton bands is not essential. Even for the characteristic exciton band, the orbit of the excited electron may largely extend over the nearest neighbouring ions or may even be deformed by the electric fields in such a way that the excitation takes a large amount of transfer character. Therefore all these bands are called exciton bands, while the continuum arising from the intermingling of bands of the type A (B), A (A^{2+}), etc., contains so called ionisation levels or conduction levels. Whether the non-conducting exciton levels really exist below the conduction levels depends largely on the constitution of the ionic lattice. If the atoms are pushed together sufficiently the exciton levels may also be taken up in the continuum.

3.3 *The crystal orbit approximation*

Starting with the approximation of atomic orbits in which the effect of place exchange was neglected, we have been able to discuss the effect of the electrostatic interaction of the electrons on the excited states of the crystal as a whole. Afterwards we have introduced the effect of place exchange on the levels of a crystal as a whole. We have stated that the result was a number of exciton bands in which the crystal shows no electric conductivity, and a number of ionisation levels in which the crystal is conducting. In the case of the exciton bands this method of approximation was suitable in giving an idea of the electronic excitation processes giving rise to these bands, while it also showed why the crystal is non-conducting in these states. In order to see more clearly

how the conducting property of the ionisation levels comes into existence it is preferable to use a different starting point of approximation: the crystal orbit approximation.

In this approximation each electron is assumed to occupy a crystal orbit which extends through the whole crystal (BLOCH wave). In each orbit the velocity with which the electron travels through the crystal is well defined, but it is impossible to indicate the place of the electron. Evidently, the place exchange is largely accounted for in this approximation. The energy of the individual orbital levels can be defined again as the energy required to remove an electron from the orbit to infinity. If we remove an electron from a crystal in its ground state, the energy required depends on the kinetic energy which the electron originally had in the crystal. In other words the energy to remove an electron cannot be given by one single value, and in the energy scheme we obtain a band of levels from which the electron could be removed instead of one sharp level. In this way the A^+ and B^- bands of Fig. 1*c* are found, in the levels of which the electrons principally move along the A^+ and B^- ions respectively (tight binding). The former band is the narrower because the effect of place exchange is smaller for the valency electrons of A^+ ions than for those of the B^- ions. If the place exchange would tend to zero these bands would shrink together to the A^+ and B^- levels in our atomic orbit scheme.

In an insulating crystal in its ground state the A^+ and B^- bands are fully occupied by electrons and the exact theory shows that conductivity is not possible since there are always as many electrons moving in one direction as in the opposite direction. But now we can excite an electron into one of a large number of excited crystal orbits. Groups of levels in which excited electrons move with different energies along the A^+ or B^- ions, form together the A and B^{2-} band respectively. The excitation process can be described by the raising of an electron from a level of one of the normally full bands into a level of the empty A band or B^{2-} band. In such an excited state of the crystal as a whole conduction is possible both by the travelling of the excited electron and by the

travelling of the electronic "hole" that is created in the originally full band by the removal of the electron. Which of these two conduction mechanisms predominates depends on the place exchange or — and this is closely related to it — on the width of the bands which define the energy of the electron and the hole. Usually the empty A and B^{2-} bands are wider than the occupied A^+ ad B^- bands. Then in most cases an electric current is predominantly carried by the excited electrons. In this connection the empty bands are called conduction bands.

The position of the A and B^{2-} band corresponds more or less to these levels in the atomic orbit scheme. If the place exchange would tend to zero the excited A and B^{2-} bands would shrink together to the series limit of the A (B) or A (A^{2+}) levels and of the B^{2-} (A^{2+}) or B^{2-} (B) levels respectively in the atomic orbit scheme. This is correct because the levels, though derived in a different way, indicate similar situations: In the atomic orbit picture an electron in a level at one of the series limits of transfer transitions is an electron which is situated at a fixed position at a large distance from its equally fixed hole. In the crystal orbit picture excited electrons and their holes moving independently through the lattice, may occasionally come very near to one another, but on the average the distance between electrons and holes will be large, and accordingly an excited electron may also be considered as being far from its hole.

Since the crystal orbits extend through the whole crystal, while the place of an electron or a hole in a crystal orbit is completely undetermined, it is impossible to describe a state in which an electron and a hole are bound together (exciton) by means of an electron and a hole both occupying a crystal orbit. Therefore it would be misleading and incorrect to draw exciton bands in a figure like Fig. 1*c*. For the same reason an energy scheme of the levels of the crystal as a whole, constructed from the energy values of the individual crystal orbit levels, can only give information on the position of those states of the crystal which we have called ionisation levels, but it completely ignores the existence of non-conducting

excitation states. The absence of exciton states from the energy schemes derived in this way essentially arises from the fact that in the energy values of the individual levels of the crystal orbits only a part of the electrostatic interaction of the electrons can be accounted for (namely that part of the interaction which can be described by some mean value, i.e., the periodic potential field in which an electron in an orbit is assumed to move). It is possible to investigate the effect of the complete electrostatic interaction on the levels of the crystal as a whole such as they were obtained from the crystal orbit scheme. This has been done by WANNIER [1] and he was able to show that exciton bands must indeed be expected to exist below the ionisation levels (energy scheme of the crystal as a whole!). This is in accordance with the fact that, whether we start with atomic orbits or with crystal orbits, the same states for the crystal as a whole should be obtained, providing the approximations are carried out far enough.

The result of WANNIER does not mean, however, that it is allowed to introduce exciton bands into an orbital energy scheme like Fig. 1*c*. The allowance for complete interaction essentially excludes the use of a scheme of this kind [2].

3.4 *The influence of vibrations*

All the energy states discussed have been derived for crystals in which the constituents are at rest. In reality, however, the ions will vibrate owing to thermal motions (including zero-point vibrations), while further vibrations may be excited in some other way, generally by processes in which energy is dissipated (cf. Section 8.1). These vibrations affect the energy levels in

[1] G. H. WANNIER, *Phys. Rev.*, **52** (1937) 191.

[2] The situation is comparable to the one which we met in the derivation of the energy states of a crystal with the aid of atomic orbits. There the orbital energy scheme obtained as a first approximation (Fig. 1*b*) had more or less an exciton character; introduction of place exchange leading to energy bands and conductivity was only possible in the scheme of the crystal as a whole (Fig. 2*a* → 2*b*). Here on the contrary the orbital energy scheme obtained as a first approximation has a band character (Fig. 1*c*) while a further approximation, equally being only possible in the scheme of the crystal as a whole, leads to the appearance of exciton states.

two ways. In the first place the existing levels are blurred due to the fact that the electric field of the lattice is no longer constant at a certain point, but varies in the time as regards intensity as well as symmetry. In the second place the electronic states (and accordingly also the states of the crystal as a whole) occur combined with the various vibration states, resulting in a multiplication of levels, the intervals corresponding to the vibration frequencies.

4. ABSORPTION IN PURE CRYSTALS

In the previous section we have discussed the various transition processes which may occur in a crystal. The energy required for a transition may be obtained from radiation. The frequency of the radiation which is absorbed by the crystal, is determined by the relation $\nu = \Delta E/h$, where ΔE is the energy difference between the ground state and an excited state of the crystal. The actual absorption spectrum, i.e., the distribution of the absorption strength over the spectrum is not determined by the position of the excited states alone, but also by the relative magnitude of the transition probabilities for the various transitions. Certain transitions will be forbidden for optical excitation. On the basis of the orbital picture we should expect a number of absorption lines, caused by the transition of an electron from an occupied into an unoccupied orbit [1]. Pure excitation processes and transfers to nearest neighbours will have a large transition probability and these absorption lines will also keep their individuality when place exchange is taken into account. In order to see how the transition probabilities are distributed for transitions from the ground state of the crystal into its "ionisation levels", we can better make use of the crystal orbit picture. Here the selection rule for an optical transition between an occupied and an unoccupied orbit is that in both orbits the electron

[1] It will be clear that, in consequence of the definition of the orbits, not every arrow between an occupied and an unoccupied level has a meaning. For instance it is meaningless to speak of the transition from the A^+ into the B^{-*} level.

must have the same momentum. Since each particular level of an energy band in the orbital picture is characterized by a particular momentum, the selection rule restricts transitions to those occurring between corresponding levels. The relation between the energy of the levels and the momentum is however not simple. The upper level of a band may correspond to the largest momentum and the lower level to the smallest momentum, but the reverse may occur as well, and more complicated relations may also occur [1]. Since this relation may further be different for the various bands, the result is that the width of the absorption band for transitions into ionisation levels is at most equal to the sum of the widths of the crystal orbit bands involved, but will generally be narrower.

The absorption will be differently named according to the electronic process underlying it. Absorption in which both kinds of the constituents of the crystal are involved, viz., absorption connected with a transfer transition between orbits of ions of mostly opposite sign will be called *lattice absorption* or *fundamental transfer absorption*. When an excitation may be interpreted as being associated with an electronic transition between two orbits of one and the same ion, we shall speak of *ionic absorption* or *characteristic absorption*.

The long wave-length limit of the absorption of a crystal is determined by the cheapest transition, i.e. the transition that costs least energy; in the case shown in Fig. 2*b* it is the transfer of an electron from a negative ion B^- to a positive ion A^+. When a separate excited state (exciton state) exists below the conduction band — and this is assumed in Fig. 2*b* — the cheapest transition is the transition from B^- to an adjacent A^+ ion. This is probably realized in sodium chloride [2]. It may be, however, that the exciton states are submerged in the conduction band. The cheapest transition then corre-

[1] Cf. N. F. MOTT–H. JONES, *Properties of metals and alloys*, Oxford (1936).

[2] J. N. FERGUSON jr., *Phys. Rev.*, **66** (1944) 220. Photo-conductivity was observed upon irradiation into the fundamental absorption beyond a certain limit; irradiation into the first peak did not cause conductivity.

sponds to a liberation of electrons. This seems to be the case with the iodides of sodium and potassium [1].

Absorption bands corresponding to the other transitions are situated at shorter wave-lengths. Due to the width of the various energy bands the absorption spectrum consists of a broad region filled with overlapping absorption bands, with only here and there indications of a maximum (Fig. 2*b*). Since the absorption coefficients in these bands are very high, the structure can only be found experimentally by working with extremely thin layers. With normal powders, consisting of particles with a diameter from 1—50 μ we only observe a continuous absorption region, with a more or less sharp limit at the long wave-length end. In this case bands correlated with a possible excitation of ions $A^+ \rightarrow A^{+*}$ or $B^- \rightarrow B^{-*}$ cannot be observed because they are submerged in the strong lattice absorption. When however the characteristic excitation of ions costs little energy, as is realized in the "coloured" ions of the transition elements, the rare earths, etc., it may so happen that these excitations cost even less energy than the cheapest fundamental absorption. Then we observe some comparatively sharp characteristic absorption bands at the long wave-length side of the fundamental absorption region. Single negative ions of the coloured type do not exist: whenever negative ions give rise to a characteristic absorption, they are complex (e.g., NO_3^- or $WO_4^=$) and accordingly the absorption bands are not so sharp as with the coloured positive ions [2].

[1] W. Poddubny, *Acta physico-chem.* U.R.S.S., **9** (1938) 712; *J. Exptl. Theor. Phys. U.S.S.R.*, **8** (1939) 410. Irradiation into the entire fundamental absorption caused photo-conductivity while the spectral distribution of the absorption and the response of conductivity were practically identical.

[2] We could think of working with single ions instead of with complex ions, e.g., in $NaNO_3$ with Na^+, N^{5+}, O^{2-} instead of Na^+ and NO_3^-. The use of complexes is justified by the fact that the same complex units are found in different substances while, further, the binding between the central ion and the surrounding oxygen bears a covalent character, so that a purely electrostatic model is not satisfying. It may be emphasized, however, that the *characteristic* absorption of such a complex ion may well be a *transfer* transition between different constituents of this complex ion.

Therefore, when the excitation of these complex negative ions costs less energy than the fundamental absorption of the crystal, we find a broad absorption band with a long wavelength limit not much sharper than must be expected for transitions of the fundamental type. Only by special investigations are we able to prove that the absorption edge must be attributed to a characteristic transition within the complex negative ions. In contrast to the characteristic transition, transitions of the fundamental type $B^- \rightarrow A^+$ are very sensitive to changes in the lattice dimensions. Systematic study of the behaviour of the edge in mixed crystals therefore provides one of the methods of identification. We may also study the absorption of a series of substances in which the ion under consideration remains the same but the ion of opposite sign is varied. For instance, in various tungstates we always find the absorption edge at nearly the same wave-length in the near ultra-violet, indicating that in these substances the process determining the absorption edge is an electronic transition within the tungstate group.

Pure lattice absorptions have been found with a large number of simple compounds as *NaCl, ZnO, AlN, MgS*, etc. A quantitative agreement between the experimentally determined positions of the absorption edges and the calculated values can only be expected to be satisfactory in cases in which the binding character of the crystals fulfills the fundamental assumption underlying the calculations, viz., that it be almost entirely ionic. This is realized to a certain extent with the alkali halides and earth alkali halides [1]. For substances in which covalent forces contribute considerably to the binding, as is probably the case for *ZnS, CdS, ZnSe, ZnO* [2], the agreement is rather poor [3]. Characteristic absorptions of

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[1] J. H. DE BOER, *Z. f. phys. Chem.* (B), **18** (1932) 49.
W. KLEMM, *Z. f. Phys.*, **82** (1933) 529.
L. M. SHAMOWSKY, *J. Phys. Chem.* U.S.S.R., **13** (1939) 835.
K. BUTKOV–I. WOJCIECHOVSKA, Nature, **159** (1947) 570.

[2] M. BORN–GÖPPERT MAYER, *Handb. d. Phys.*, **24** (II) p. 734.
F. A. KRÖGER, *Chem. Weekbl.*, **37** (1940) no. 45; *Z. Kristallogr.*, (A) **102** (1939) 132.

[3] F. SEITZ, *Modern Theory of Solids*, New York–London **1940**,

positive ions next to the fundamental absorption are observed with salts of the rare earths and the transition elements, while absorptions due to complex negative ions occur with nitrates, tungstates, chromates, manganates, molybdates, a.o.

Recently Uehara has carried out calculations of the absorption edge in which he has corrected for covalency [1]; satisfactory agreement seems to have been obtained for alkali halides and hydrides [2], thallium halides [3], copper hydrides [4], and alkaline earth sulphides [5] and oxides [6].

5. THE LEVELS OF PERTURBED CRYSTALS

The introduction of a foreign atom into the lattice gives rise to new levels in our schemes. We shall consider first the atomic orbit approximation. The outer electron of the foreign atom or ion occupies an orbit, called C in Fig. 3 [7] (*a* and *b*). The orbit must be situated in our orbital scheme somewhere below the lowest empty transfer level of the matrix crystal. This condition must be fulfilled, because otherwise a spontaneous transfer of the electron from the C orbit to one of the lattice ions would occur and the C orbit would not be occupied in the ground state. (Chemically this means that the ion would spontaneously change its valency state).

A number of excited orbits may belong to the C orbit, for instance an orbit C*, occupied only after a characteristic excitation of the foreign ion, and two series of transfer states A (C^+) and B^{2-} (C^+), which will be occupied after the transfer of an electron from the C orbit to one of the lattice ions A^+

p. 448; for measurements of the fundamental absorption of *ZnS*, *ZnO*, *CdS* and *CdO*, cf. E. Mollwo, *Reichsber. f. Phys.*, **1** (1944) 1.

[1] Y. Uehara, *J. Chem. Soc. Japan*, **63** (1942) 587;
[2] *ibid.*, 597;
[3] ,, 1019;
[4] ,, 1041;
[5] ,, 1310;
[6] ,, **62** (1941) 1270.
All these articles have been referred to in *Chem. Abstr.*, **41** (1947) 2993.

[7] States like A^+ which are not involved in the optical transitions in which we are interested have been omitted from this figure.
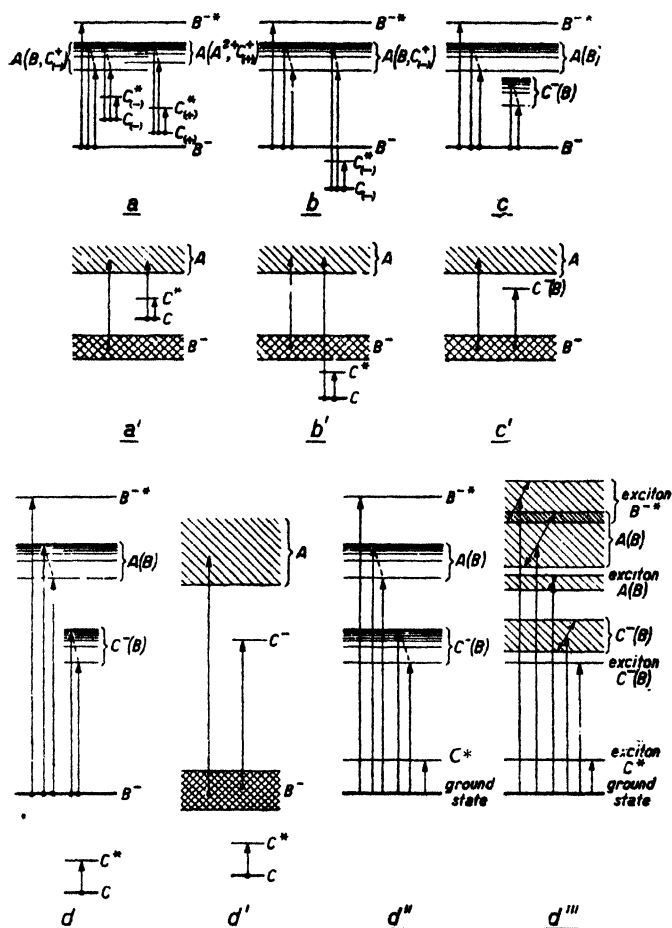
Fig. 3.

a, b, c, d: Four possible atomic orbit energy schemes of a perturbed crystal with (*a*, *b*) occupied, (*c*) empty, and (*d*) both occupied and empty levels of the foreign ion.

a', b', c', d': Energy band pictures corresponding to the orbital schemes *a, b, c, d*.

d'' and *d'''*: Energy schemes of a crystal as a whole for the system described by *d* and *d'*, without and with allowance for electronic exchange.

or B^-. The series limits are of course the same as those for the A and B^{2-} transfer series defined earlier. In the case of a foreign ion of substitutional type, the A (C^+) orbits will have the same energy as the A (B) or A (A^{2+}) orbits, depending on the kind of ion that was replaced by the C ion, and in the same way the B^{2-} (C^+) orbits will have the same energy as the B^{2-} (B) or B^{2-} (A^{2+}) orbits. In Fig. 3*a* we have drawn the A (C^+) levels for the case that C is a positive ion $C_{(+)}$ or a negative ion $C_{(-)}$. The foreign ion may also introduce empty orbits in our orbital picture, i.e., orbits to which electrons may be transferred from lattice ions. For reasons similar to the ones discussed above, the levels of these empty orbits must be situated above the upper occupied lattice level. In Fig. 3*c* we have drawn them in such a way that it costs less energy to lift an electron from a B^- ion into the orbit of the foreign ion than into the A (B) levels. The series of empty C^- (B) orbits which have been drawn must be understood in the same way as the transfer series A (B) of the pure lattice. Although the electron is always excited to the same orbit with respect to the C^- ion, the energy required for the excitation depends on the distance at which the ion is situated from which the electron was removed and where it leaves behind an electronic hole.

Obviously in reality both empty and occupied states and characteristic excited states occur together in one system. In Fig. 3*d* we give a possible configuration.

The level schemes of the crystal as a whole may be obtained from the atomic orbital pictures in the way as was discussed for the pure crystals. In Fig. 3*d″* this has been carried out for the system whose atomic orbit energy scheme was shown in Fig. 3*d*. The lowest excited state corresponds to characteristic excitation of the foreign ion $C_{(-)}$, then follow the states corresponding to transfer of electrons from B^- ions to the foreign ion and to A^+ ions and finally the excitation of the B^- ions.

Electronic place exchange causes the transfer levels of the base lattice to merge into a band, only levels corresponding to transfer transitions between neighbouring ions retaining their individuality (exciton states). The excitation levels of

the foreign ion, however, remain sharp because the mutual distance between the various foreign ions is so large that electronic place exchange may be neglected (Fig. $3d'''$).

Usually the phenomena of luminescence and absorption are described with the aid of a crystal orbit scheme. Fig. $3a'$, b' and c' show this kind of scheme for the situations which have already been described with atomic orbits in Fig. $3a$, b and c. Fig. $3a'$ and b' apply to situations in which the foreign ions give rise to occupied levels C. The occupied and unoccupied levels of the constituents of the matrix lattice form bands. The energy of the occupied C-levels is sharp because there is no electronic place exchange between the various C ions[1]. All transfer processes indicated in the figures, namely the transitions between the B^- band and the A band or between the C level and the A band, are processes in which the excited electron is removed far from the hole it leaves behind. We have also drawn a characteristic excited state of the foreign ions. Although similar excited states of the constituents of the base lattice cannot be indicated (cf. Section 3.3), the indication of such excitation levels of the foreign ion is allowed; the reason is that both the orbits of the ground state and the excited state of the foreign ion are of the atomic type (cf. note).

Fig. $3c'$ shows a situation in which the foreign ion can accept an electron. Also for this case only these transfer states can be indicated in the scheme, in which the excited electron has been brought to a large distance from its hole. The corresponding excitation processes are indicated by arrows. The energy of the normally unoccupied C^- level, defined by the energy required to remove an electron from the foreign ion after it has taken up an electron (C^-), is sharp again because of the lacking place exchange.

So far we have only discussed the effects of an extremely small amount of foreign ions. If the amount of foreign ions

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[1] A description of states with the aid of crystal orbits has hardly a meaning for foreign ions present in a small concentration. The C-orbits do not extend through the whole crystal, and are of the atomic rather than of the crystal orbit type.

incorporated in the crystal becomes considerable, the lattice constant of the crystal will be changed and with the lattice constant the electrostatic interaction of the ions. An increase of the lattice constant so causes the levels of the positive ions to fall and those of the negative ions to rise (cf. Section 3.1). As may be seen from Fig. 1*b*, the extent to which the energy is changed is different for different kinds of levels. Ground states and characteristic excited states are changed by an amount $(Me^2/r^2)\,dr$, excited states which are reached by a transfer transition ending at a negative ion rise by $(Me^2/r^2 + e^2/rR)\,dr$, while those ending at a positive ion fall by $(Me^2/r^2 - e^2/rR)\,dr$. Hence the characteristic processes are not affected by the expansion in this approximation. The energy required for transfer transitions between ions of the same sign (from A^+ to another A^+, or from B^- to another B^-) increases, solely as a consequence of the interaction between the excited electron and the hole it leaves behind, by $(e^2/Rr)\,dr$. The energy of transfer transitions from positive to negative ions increases very rapidly by $(2Me^2/r^2 + e^2/rR)\,dr$. The only processes which become cheaper by the expansion of the lattice are the transfer transitions from negative to positive ions, the energy of which decreases by $(2Me^2/r^2 - e^2/rR)\,dr$.

Obviously such effects accompany expansion or contraction of the lattice quite generally, independent of whether the change is caused by the formation of mixed crystals as discussed above, or by temperature or a high pressure.

6. PRIMARY, SECONDARY, DIRECT AND INDIRECT EFFECTS OF ADDED IONS; ACTIVATORS

In considering the levels caused by the incorporation of a foreign ion or an additional lattice ion in the energy scheme of a system, we must not only pay attention to the incorporated ion itself, but also to the chemical changes in the lattice induced by its presence. A good example is provided by the formation of F-centres in the alkali halides. When alkali halides are heated in alkali vapour, an excess of alkali is dissolved in the crystals. It has been supposed at first that the alkali was

incorporated as alkali atoms. Gradually it has become clear, however, that this is not the case. At the temperature at which the alkali is able to enter the crystals, the stable configuration of the alkali halide crystal is not a perfectly built crystal, but it is a crystal containing a certain amount of open positions for both positive and negative ions [1]. The excess of alkali entering the crystal on heating in alkali vapour is incorporated as normal positive ions at lattice positions, thus changing the equilibrium between occupied and unoccupied positions of both kinds in such a direction that the relative concentration of alkali holes is diminished and that of the halide holes is increased. The electrons, which must enter the crystal together with the alkali ions in order to maintain electro-neutrality, are bound at the unoccupied halide positions. It is these trapped electrons, and not the alkali itself, which are held responsible for the colouring observed [2].

Similar effects may be expected in corresponding cases where an excess of one of the constituents of the lattice is present, as, for instance, *Zn* in *ZnO* [3], and also in systems where foreign ions of a different valency are incorporated: S^{2-} or O^{2-} and Ba^{2+}, Sr^{2+} and Ca^{2+} in *KCl* [4]. Effects of this kind probably occur more generally than is usually realized. A considerable part of the luminescence effects shown by oxides, sulphides and selenides of *Ca, Sr, Ba, Mg, Zn, Cd* must probably be interpreted with the aid of levels of this kind.

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[1] W. Schottky, *Naturw.*, **23** (1935) 656; *Z. physik. Chem.* (B), **29** (1935) 335.
W. Jost, *Z. techn. Physik*, **16** (1935) 363.

[2] J. H. de Boer, *Rec. trav. chim. Pays-Bas*, **56** (1937) 301.
N. F. Mott, *Trans. Far. Soc.*, **34** (1938) 822.

[3] O. Fritsch, *Ann. Phys.*, **22** (1935) 375.
H. H. von Baumbach–C. Wagner, *Z. physik. Chem.* B, **22** (1933) 199.
P. H. Miller jr, *Phys. Rev.*, **60** (1941) 890.
F. Seitz, *Modern Theory of Solids*, New York–London (1940) p. 192, 464.
N. F. Mott–R. W. Gurney, *Electronic Processes in Ionic Crystals*, Oxford (1940) p. 165.

[4] S. Akpinar, *Ann. Phys.*, **37** (1940) 429.
H. Pick, ,, ,, **35** (1939) 73.

From a physical point of view the incorporated ion and the secondary chemical variations of the lattice caused by it are perfectly equivalent. Both manifest themselves in two ways: In the first place directly, in the second place indirectly by changing the physical conditions (strength and symmetry of the electric field, polarisability, repulsion) for the adjacent lattice ions. As we saw in the previous section that each perturbation in the lattice causes the occurrence of localized energy levels, we have to deal with four kinds of such localized levels in the energy scheme:

1. levels belonging to the incorporated ion itself.
2. ,, ,, ,, the holes or to lattice constituents of changed valency, secondarily caused by it.
3. ,, ,, ,, lattice ions, perturbed by the presence of the incorporated ion.
4. levels belonging to lattice ions, perturbed by the secondary changes caused by the incorporated ion.

When the incorporated ion is a foreign ion of the same valency and nearly the same ionic radius as the lattice ion for which it is substituted, the perturbation will be small and accordingly the levels of kind (3) will hardly differ from the normal lattice levels. When however these conditions are not satisfied, the perturbed lattice levels may differ considerably from the normal lattice levels. As an example we may give KCl containing a small amount of $SrCl_2$ in solid solution. In this mixed crystal the levels of chlorine ions occupying positions next to the divalent strontium ions are about e^2/r lower than the levels of the chlorine ions which are normally surrounded by monovalent potassium ions, the strontium ion behaving like an extra positive charge. In the same way an unoccupied lattice position behaves like a charge of the same magnitude as that of the missing ion, but with opposite sign, and so perturbs the levels of its neighbours, giving rise to levels of the type mentioned as (4).

If any of the levels associated with the incorporation of a foreign ion play an essential part in the luminescence shown

by a system, we speak of activation, the ion being called activator. We propose to call the ion primarily introduced into the lattice a *primary activator* or briefly the *activator*, and any active chemical consequences of its presence a *secondary activator* [1]. So in additively coloured alkali halides the excess of alkali dissolved in the crystals is the primary activator, while the halide holes formed, together with the electrons trapped at them are secondary activators.

When at least one of the levels involved in the optical processes associated with the primary or secondary activator belong to the activator itself (levels of type 1 and 2) we may speak of *direct activation*. When, however, only the perturbed lattice ions near the (primary or secondary) activators are essential for the luminescence (levels of type 3 and 4) we may speak of *indirect activation*. Examples of direct activation in which the entire emission process takes place within the activator and in which obviously both the starting and the ending level of the transition belong to the activator, are provided by systems activated by rare earths, like *MgO–Sm*, *CaS–Eu*, etc. *ZnS–Cu* is probably an example of direct activation in which only one of the levels involved in the emission belongs to the activator (the *Cu* ion), the other one belonging to one of the neighbouring lattice ions. Systems for which it has been proved that indirect activation occurs are not yet available. That such a kind of activation is possible in principle, however, has been shown by KLASENS [2]. Let us consider for instance the situation existing in an alkali halide crystal in the neighbourhood of an unoccupied negative position. Such a negative hole has the effect of an extra positive charge at the same position and causes the levels of the neighbouring ions to fall. Now the nearest positive ions, occupying positions next to the hole, are closer to it than the nearest negative ions, so that the levels of the first ions are lowered more than those of the latter ions. Therefore the transfer

[1] Here we differ from some authors who reserve the latter name for cases in which a luminophor contains two activators or an activator together with a sensitiser. We propose to speak in these cases of *double activation* and *sensitization*.

[2] H. A. KLASENS, private communication.

transition from a negative ion to a positive ion in the neighbourhood of the hole is cheaper than the corresponding transition in the normal undisturbed lattice. And, since the latter is the one which determines the long wave-length edge of the fundamental absorption, the perturbed process causes an absorption (and an emission corresponding to it) at the long wave-length side of this edge (cf. Section 7).

Localized levels may further be involved in other processes: they may cause extra absorption — poisoning, sensitization (cf. Section 10) — or they may furnish metastable states for the phosphorescence process (cf. Section 8.2). The nature of all these levels is the same; which of the various physical processes in which they may be involved predominates depends on such additional conditions as temperature, the presence of other levels, etc.

7. ABSORPTION IN ACTIVATED CRYSTALS

The absorption spectrum of a crystal whose energy scheme contains localized levels due to primary, secondary, direct or indirect activation consists of the normal lines or bands of the matrix lattice together with bands or lines due to the activation. The electronic transitions may be seen from the energy schemes discussed in the previous section (Fig. 3). The absorption bands caused by the activation are either of the characteristic type, occurring between two localized levels of the same ion, or of the transfer type, taking place between a localized level and a level or band of the matrix lattice. Just as we have seen for the sharp characteristic absorption bands in pure crystals, the relatively faint absorptions connected with the localized levels are only to be observed when the energy of the particular transitions is smaller than the energy necessary for the processes which give rise to the broad and strong absorption bands of the base crystal (Fig. 3*a*, *c*). If this condition is not fulfilled, the additional bands are completely submerged (Fig. 3*b*, $C_{(-)} \rightarrow A$).

Transfer transitions between perturbed and unperturbed lattice ions may be observed as a long wave-length extension

of the fundamental absorption. Characteristic transitions in incorporated foreign ions are easily identified as such. Characteristic transitions in perturbed lattice ions may be distinguished from the corresponding transitions in the normal lattice ions because of the fact that the excited state will probably be perturbed to a greater extent than the ground state. When more than one characteristic process occurs in one ion, an additional effect may be caused by a variation in the transition probabilities of these various transitions, resulting in a variation of the proportion in which they occur.

If the cheapest transition in the matrix lattice is the fundamental transfer transition, the activator absorption is observed at the long wave-length side of the fundamental absorption (Fig. 3*d*). This is realized in *ZnS–MnS*. When it is a characteristic transition, the activator absorption occurs at the long wave-length side of the characteristic absorption band. This is the case in $CaWO_4$–*Sm*.

Incorporation of a considerable amount of activator or formation of mixed crystals with another additional compound, in general will cause a variation of the lattice constants. As we have seen in section 5, this variation causes a change in the relative position of the levels. Characteristic absorptions remain unchanged. Absorptions due to transfer transitions between ions of corresponding sign, or due to transfer transitions from a positive to a negative ion, will shift: towards the violet if the lattice is widened, towards the red if it is contracted. On the other hand absorptions associated with transfer transitions from a negative to a positive ion, i.e. the kind of transitions which normally cost the least energy and determine the absorption edge, are shifted in the opposite direction. This difference provides a method to distinguish between the various kinds of absorption processes.

From the foregoing it will be clear that no differences exist in principle between the characteristic ionic absorption for a pure substance and for an activated substance. In cases where the matrix compound and the corresponding activator compound are able to form an uninterrupted series of mixed

crystals a continuous change from one type to the other may occur. For instance the properties of LaF_3 activated by CeF_3 change continuously into these of pure CeF_3 with increase of the cerium fluoride content [1]: CeF_3 may be considered as a substance containing 100% activator.

A similarity of the same kind exists between the fundamental absorption of pure crystals and one of the transfer absorptions possible in activated crystals, viz., the one corresponding to an electronic transition between a normally incorporated activating ion and a mostly oppositely charged constituent of the matrix lattice. It is reasonable therefore to speak in the latter case of the fundamental absorption of the incorporated activator compound. With ZnS–MnS [2] and Zn_2SiO_4–Mn_2SiO_4 [3] the different types of transitions occur together.
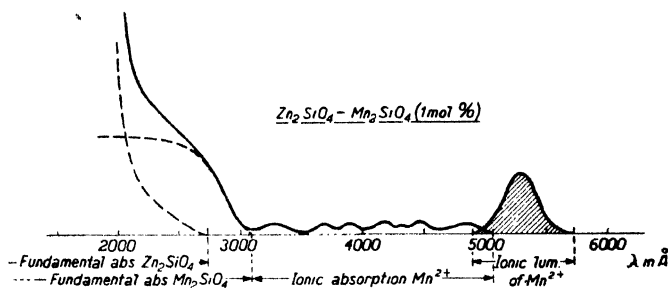
Fig. 4. A schematic drawing of the regions of absorption and emission of Zn_2SiO_4 — 1 mol % Mn_2SiO_4.

In the latter case, for instance, we observe the fundamental absorption of the matrix lattice Zn_2SiO_4 with an edge near 2250 Å and the fundamental absorption of the incorporated Mn_2SiO_4 with a long wave-length limit at about 3000 Å; in addition a characteristic ionic absorption of Mn^{2+} is found consisting of narrow bands between 3000 and 5000 Å. A

[1] F. A. Kröger–J. Bakker, *Physica*, **8** (1941) 628.
[2] F. A. Kröger, *Physica*, **6** (1939) 779.
[3] F. A. Kröger, *Physica*, **6** (1939) 764.

schematic drawing ofth is absorption spectrum, together with the emission spectrum yet to be discussed, is given in Fig. 4 [1].

Obviously this absorption spectrum corresponds with an energy scheme as shown in Fig. 3*d* .... *d'''*.

8. EMISSION OF PURE CRYSTALS AND OF ACTIVATED CRYSTALS [2]

Every statement made up till now about the absorption of light by a crystal applies almost unchanged to the emission. The only difference is that while the absorption process has the ground state as its initial state and is normally always possible, it is necessary for the occurrence of emission that the crystal be excited, i.e, an electron must have been brought from one of the occupied lower levels to one of the empty upper levels. In the energy schemes the emission may be indicated by arrows pointing downwards.

Although absorption and emission are in principle the same processes occurring in opposite directions, the wave-lengths of absorption and emission are usually not identical. This is a consequence of a principle which is generally known as the FRANCK–CONDON principle.

This principle states that wave-lengths and intensities of emission and absorption lines should be derived on the assumption that during an electronic transition the ions do not change their position. If the equilibrium position is the same for the ground state and the electronic excited state, the wave-lengths of absorption lines and of corresponding emission lines are identical. When the equilibrium configuration of the ions in these two states is different, however, this is not true. We

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[1] Absorption curves recently measured by CHUNG KWAI LUI, *J. Opt. Soc. Am.*, **35** (1945) **492** show a different distribution of absorption strength over the spectrum, the absorption in the short wave-length region being smaller than is indicated in Figure **4**.

[2] In this section we only discuss the energetical situation, i.e., the position on the wave-length scale of the emission with respect to the absorption. Whether emission will actually occur or not depends on further conditions.

shall discuss this case with the aid of figure 69*a* (p. 211), in which the energy of the electronic ground state and the electronic excited state have been given as a function of a certain generalized coordinate, describing the positions of all the ions of the lattice with respect to one another. In this scheme the invariability of the ionic configuration during an optical process restricts such processes to vertical transitions between the two curves. Therefore in the excitation process starting from the vibrationless ground state A, the system does not arrive in the vibrationless state B′ of the electronic excited state, but in the vibration state A′ for which the initial atomic configuration happens to be a possible configuration. If the lifetime of the electronic excited state is extremely short, the electron will fall back with the emission of a radiation identical in wave-length with the absorption (resonance fluorescence A′ → A). If the lifetime of the electronic excited state is somewhat longer, however — and this is what usually seems to be the case — the vibration energy of the excited state is transferred to the surroundings before the electron returns to the ground state. The crystal then takes up the state B′ in which the atoms are at rest in the configuration which is stable under the new circumstances. From this state, the electron now may fall back. Just as for the absorption, the crystal does not arrive in the vibrationless ground state, but at the vibration state B of the electronic ground state. Accordingly the absorption process A → A′ costs more energy and hence involves larger quanta, the emission process B′ → B yields less energy and involves smaller quanta than would correspond to a direct transition between the vibrationless states A and B′: the emission is displaced towards longer wave-lengths with respect to the corresponding absorption.

This effect will be large when the rearrangement is considerable, as will be the case when the optical process is accompanied by a displacement of charge (transfer processes, excitation of complex ions); it will be small when the rearrangement is small (characteristic processes within single ions).

The FRANCK–CONDON principle, however, is not the only reason for a displacement of the emission with respect to the absorption. If several different excited states exist, the emission may be the electronic transition from a high excited state to a lower excited state. Such intermediate excited states may easily escape our attention if they are so low that the absorption corresponding to the transition from the ground state to these states occurs in the infra red. This situation is for instance realized with terbium [1].

9. FLUORESCENCE AND PHOSPHORESCENCE

The essential electronic transitions of absorptions and the corresponding emissions are, in the first instance, independent of the temperature. Therefore the simplest emission processes, in which the emission directly follows the absorption with which it corresponds are also independent of the temperature. The emission process may be more complicated however, and involve intermediate states. It may for instance so happen that an excited state exists below the normal excited state which is reached in the excitation process. Instead of returning to the ground state, the system may fall to this intermediate state (Fig. 5A). It may leave this state in two ways:

1. it may directly return to the ground state, giving rise to an emission not corresponding to the initial absorption (process β).
2. it may be lifted up to the initial excited state and then may return to the ground state with the emission of a radiation which corresponds to the initial absorption (process α).

The second process will only occur to an appreciable extent when the transition probability for the first process is not too high. Then the intermediate state has a long lifetime and may be called a metastable state.

The first process is independent of the temperature. In the second process, however, the raising of the system from the

[1] A. SEIDEL, J. LARIONOV, A. FILIPPOV, *J. of Physics*, **1** (1939) 67; *J. Exp. Theor. Phys.*, **9** (1939) 17.

intermediate state to the excited state may be effected by thermal energy and accordingly the temperature has an essential influence on this process: at low temperature it hardly occurs, the system is frozen in; at higher temperatures the process is accelerated.
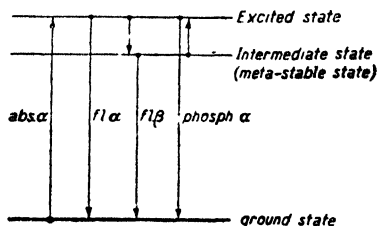
Fig. 5A. Energy levels of a phosphorescent system. (Energy of the system as a whole).

The different processes are indicated by different names. The temperature independent emissions are called *fluorescence*, the temperature dependent emissions *phosphorescence* [1]; the term *luminescence* is used for emissions when the processes are not considered in detail.

Some workers in the field of luminescence research use these terms differently, fluorescence denoting the emission of light during excitation, phosphorescence after shutting off the excitation. This distinction is however physically meaningless [2]. Like any other physical process, light emission takes its time. The emission at a certain moment is caused by the absorption at some previous moment, however short the time elapsing between the two processes may be. All emissions are afterglow in principle! The discrimination is probably intended to separate processes of long duration, predominating in the afterglow period, from processes of short duration predominating during the excitation, but the length of the time interval between the absorption of a quantum and the emission following it does not provide a basis for a well-founded

[1] F. Perrin, *Ann. Chim. Phys.*, **12** (1929) 169.
[2] P. Pringsheim, *Trans. Far. Soc.*, **35** (1939) 87.

physical discrimination. Both the temperature dependent and the temperature independent emissions may show different persistence after the ending of the excitation. In the temperature independent processes it is a property of the centre and may vary from extremely short times (10^{-8} sec for the resonance fluorescence of sodium vapour) to very long times. RIEHL [1] has proposed to call this process *spontaneous afterglow*. In the temperature dependent processes the duration is a function of the temperature. It is extremely long (and hence the intensity extremely faint) at low temperatures, extremely short (and of maximum intensity [2]) at high temperatures and is of medium duration (medium intensity) at intermediate temperatures. When temperature dependent and temperature independent processes occur together, as is usually the case, at low temperatures we have to deal almost entirely with the temperature independent process (LENARD'S "Unterer Momentanzustand"); at intermediate temperatures with both processes, the temperature dependent process being of long duration (LENARD'S "Dauerzustand") and finally at high temperatures also with both processes, but now the temperature dependent process is of short duration (LENARD'S "Oberer Momentanzustand").

On the other hand it has been proposed to use the terms fluorescence and phosphorescence for emissions related with different kinds of electronic recombination. Then fluorescence is reserved for processes in which excitation does not cause a separation of electrons from their original ions, while phosphorescence is used for processes in which excitation liberates electrons. Or in other words, fluorescence is proposed for emission processes with an exponential decay law (monomolecular processes) and phosphorescence for processes with a hyperbolic decay law (bimolecular processes). Obviously this distinction is physically well-founded and accordingly it might be applied. Yet we prefer the first definition, with

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[1] N. RIEHL, *Physik u. techn Anw. der Luminescenz*, Berlin (1941) p. 62.

[2] Provided temperature quenching has not yet set in; cf. Chapter VI.

in addition an indication of the nature of the process. So monomolecular fluorescence may indicate a temperature independent process which occurs within a centre (exponential decay), monomolecular phosphorescence may indicate a temperature dependent process in which the traps belong to the centre, while recombination fluorescence may indicate a fluorescence process in which the excited electron has been separated from the centre (hyperbolic decay law). In the same way indications of the length of the process may be useful: long-during fluorescence, short-lived phosphorescence, etc.

Yet we must realize that the distinction between fluorescence and phosphorescence is only useful in giving a rough description of the phenomena. In a more complete description the temperature dependent and temperature independent processes can not be treated separately, but they appear as special aspects of one process, the luminescence process as a whole. For ZnS luminophors such a complete description has been given by KLASENS and WISE [1].

10. THE NATURE OF METASTABLE STATES

In the preceding section we have introduced metastable states in terms of the energy of the crystal as a whole. In the orbital picture it is possible to precisize the nature of such states a little more.

In the orbital picture excitation lifts an electron from an occupied level to an unoccupied higher level. In this process the starting level becomes unoccupied and is called an electronic "hole". Intermediate states of the system as a whole now may come into existence in two ways:

1. If there exists an unoccupied level below the initially reached excited level, the excited electron may fall into it.
2. If there exists an occupied level between the excited level and the ground level, the electron occupying this intermediate level may fill the hole in the ground level, so that the hole now occupies the intermediate level.

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[1] H. A. KLASENS–M. E. WISE, *Nature* **158** (1946) 483.

The energy diagrams of these situations are given in Fig. 5B (I and II).

In general the metastable character of an intermediate state can be due to two causes. In the first place it may occur
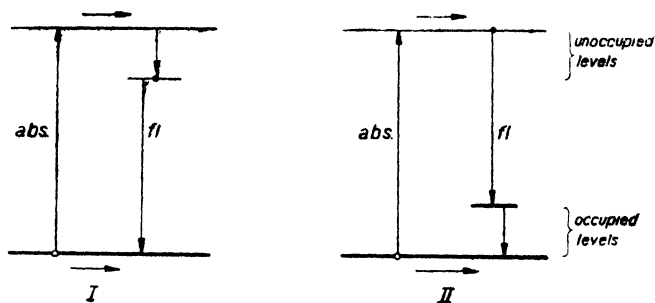
Fig. 5B. Orbital energy scheme of a crystal containing an electron trap (I) or a hole trap (II).

that the direct transition between this state and the ground state is forbidden. This is probably realized in organic molecules in which triplet states form such an intermediate metastable state [1]. Such transitions are never absolutely forbidden but the transition probability is small. Therefore the process corresponding to the direct transition from the intermediate state to the ground state is found as a faint fluorescence of very long decay (β in Fig. 5A) in addition to a strong, rapidly decaying fluorescence α and a phosphorescence of the same wave-length.

This situation may also occur in systems in which excitation separates electrons from their holes. In these cases either electrons or holes are trapped, while their counterpart (holes or electrons) remain more or less free in the normal energy bands. This is realized in Tl_2S in which incorporation of oxygen causes electron traps. Once a number of electrons have been excited and trapped, the corresponding holes remain, free to migrate through the lattice for a considerable time[2].

If the direct recombination is not forbidden, however, the

[1] G. N. Lewis–M. Kasha, *J. Am. Chem. Soc.*, **66** (**1944**) **2100**; **67** (**1945**) **994**.

[2] A. Von Hippel *and coll.*, *J. Chem. Phys.*, **14** (**1946**) **355, 370**

free components migrate through the lattice until they meet their trapped counterparts and recombination follows. In such cases a more or less stable storage of energy is only possible if the system contains both electron traps and hole
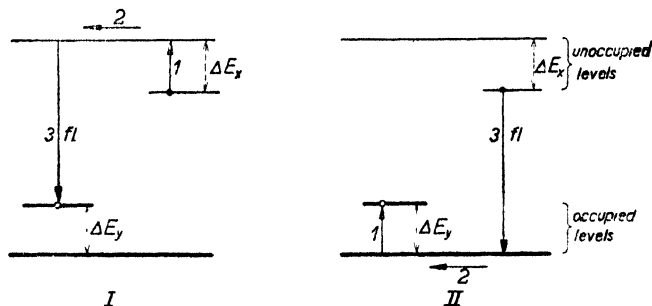
Fig. 5C. Orbital energy schemes of a system containing traps both for electrons and holes. I and II demonstrate two different ways of release of stored energy.

traps, situated at different positions in the lattice. This situation is represented in Fig. 5C.

The energy stored in such a system may be released in two ways. In the first way a trapped electron is liberated to the conduction level. It migrates through the lattice, and recombines with a trapped hole as soon as it meets one (Fig. 5C, I). In the other way the hole is liberated and migrates through the lattice, a trapped electron recombining with it when it comes close (Fig. 5C, II). Obviously the fluorescence emitted is different in these two cases (fl. I and II) [1].

Which of the two processes will occur depends on the circumstances. If the stored energy is released by temperature motion or with the aid of energy from a magnetic or electric field, the process with the smaller activation energy ΔE will predominate. If, however, the release is effected by absorption of radiation, the oscillator strengths of the two absorption

[1] The energy which is liberated in these processes may also be transferred to other centres, giving rise to different fluorescence effects.

bands corresponding to the considered transitions determine the ratio between the two processes. Each has a more or less characteristic spectral response which is determined by the relations:

$$h\nu \geqslant \Delta E_x \quad h\nu \cong \Delta E_y$$ [1].

In a number of cases the observed differences between phosphorescence and thermo-luminescence [2]) on one hand, and the glow which is stimulated by infra red radiation on the other hand may be due to this effect. *SrS–Ce–Sm* for instance shows phosphorescence in the red samarium band, but a green fluorescence due to *Ce* upon irradiation by infra red [3]. In other cases the situation is still more complicated, two kinds of hole traps being present together with electron traps. Now during the process a hole in a trap of one kind may move to a trap of the other kind. This seems to be the case in *ZnS–Mn–Cu* [4].

In the energy picture of the crystals of the type discussed here, the traps of electrons or holes are localized energy levels of the kind described in section 5 and 6. The levels are due to foreign ions, or to lattice flaws, cracks, etc. The activator may furnish one of the two necessary traps, the trap of the other kind being caused by another activator, or an ion which has no activating properties in that particular system [5]. This may

[1] The difference between the two relations is caused by the difference in width between the conduction band and the upper occupied band.

[2] Thermo-luminescence is luminescence which occurs when a system which has previously been excited at low temperatures, is heated. It is essentially the same process as phosphorescence: heat motion is responsible for the liberation of trapped electrons or holes in both cases. The only difference is that phosphorescence occurs at a certain fixed temperature, while in thermo-luminescence the temperature is increased.

[3] P. BRAUER, *Z. Naturforsch.*, **1** (1946) 70.
G. R. FONDA, *J. Opt. Soc. Am.*, **36** (1946) 382.
F. URBACH–D. PEARLMAN–H. HEMMENDINGER, *J. Opt. Soc. Am.*, **36** (1946) 372.

[4] G. R. FONDA, *Trans. Electrochem. Soc.*, **87** (1945) 339.
V. V. ANTONOV–ROMANOWSKII, *Bull. Acad. Sci.*, U.R.S.S. sér. phys., **9** (1945) 364; ref. *Chem. Abstr.*, **40** (1946) 4297.

[5] The ions found to be active in producing traps are mostly known as activators in other systems.

TABLE I

Matrix	Dominant Activator	Additional foreign ion		References
		with activating properties	no activating properties	
ZnS	*Ag*		*Gd, Tl, Pt, Os, Y*	1
,,	*Cu*		*Tl, V, La*	2
,,	*Mn*	*Cu*		2, 3, 4
ZnS, CaS, SrS	*Cu*	*Tb*		5
ZnS	*Pb*	*Cu*		6
CaS	*Pb*	*Sm*		15
SrS, Sr(S–Se)	*Eu*	*Sm, Bi Sn,*	*Fe*	7, 8
,,	*Ce*	*Sm, Bi, Sn, V, Ni*	*Fe*	8
,,	*Sm*	*Bi*		8
,,	*Mn*	*Sm, Bi Sn, Ni*	*Fe*	8
SrS	*Mn, Ce, Pr, Eu*	*Sm*		15, 16
$CaWO_4$	—	—	*	9
,,	—		*As*	10
Zn_2SiO_4	*Mn*		*As, Be, Sn*	11, 12
Zn_2GeO_4	*Mn*		*Be, Sn*	5, 12
$Zn_3(PO_4)_2$	*Mn*		*Pb*	2
$CdSO_4$	*Mn*		*Pb*	2
$CdSiO_3$	*Mn*		*Bi, Sn*	13
$Cd_2B_2O_5$	*Mn*		*Bi, Sn*	13
$Cd_5Cl(PO_4)_3$	*Mn*		*V*	14

* Heating under reducing conditions.

1. French Patent 869.336.
2. N. F. MILLER–C. E. BARNETT, *J. Opt. Soc. Am.*, **36** (1946) 352.
3. G. R. FONDA, *Trans. Electrochem. Soc.*, **87** (1945) 339.
4. V. V. ANTONOV-ROMANOVSKII, *Bull. acad. sci.*, U.R.S.S., sér. phys., **9** (1945) 364; ref. *Chem. Abstr.*, **40** (1946) 4297.
5. R. E. SHRADER–H. W. LEVERENZ–E. J. WOOD, *J. Opt. Soc. Am.*, **36** (1946) 353.
6. G. R. FONDA, *J. Opt. Soc. Am.*, **36** (1946) 352, 382.
7. R. WARD, *J. Opt. Soc. Am.*, **36** (1946) 351.
8. F. URBACH–D. PEARLMAN–H. HEMMENDINGER, *J. Opt. Soc. Am.*, **36** (1946) 351, 372.
9. S. E. SHEPPARD, *Illum. Eng.*, **10** (1917) 178.
10. A. SCHLEEDE–TIEN HUAN TSAO, *Ber. d. chem. Ges.*, **62** (1929) 767.
11. H. C. FROELICH–G. R. FONDA, *J. phys. Chem.*, **46** (1942) 878.
12. H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 199.
13. W. O. GRAFF, U.S.A. Pat. Spec., 2.400.925.
14. A. H. MCKEAG, Brit. Pat. Spec. 509.857/8.
15. P. BRAUER, *Z. Naturforsch.*, **1** (1946) 70; **2a** (1947) 238.
16. Z. L. MORGENSTERN, *C. R. Doklady U.R.S.S.*, **54** (1946) 783. V. V. ANTONOV-ROMANOVSKII, *ibid.*, **54** (1946) 19, 775.

explain the striking effects of double activation in increasing the energy storage, examples of which have been met in *ZnS–Pb–Cu*, *Sr(S–Se)–Sm–Eu*, a.o.

In Table I we have given a number of systems known to contain traps due to the incorporation of foreign ions. The ions causing the fluorescence which is predominantly stimulated by infra red have been tabulated as *dominant* activators. After the foregoing, however, it will be clear that this indication has no general value: phosphorescence for instance occurs frequently in the bands related with the other activator.

The trap-depth (ΔE, Fig. 5C) can be determined from the spectral response of the excited system to long wave-length radiation [1]. The trap-depth can also be estimated from the temperature at which thermal motion becomes active in releasing stored energy (glow curves) [2]. In both methods additional measurements are necessary to determine whether we have to do with the liberation of electrons or of holes (HALL effect). So far this has scarcely been done.

When the fluorescence system contains several electron traps or several hole traps, the occurring phenomena are more complicated. Dependent on temperature or irradation with long wave-length radiation (infra red), energy transfer or quenching (Tilgung) may occur. We shall consider such systems in Chapter VI.

11. EXCITATION OF LUMINESCENCE

The simplest cases of excitation are those in which absorption in a certain absorption band gives rise directly to the emission corresponding to it. When several of such mechanisms

[1] F. URBACH–D. PEARLMAN–H. HEMMENDINGER, *loc. cit.*
[2] F. URBACH, *Sitz Ber. Ak. Wien, Math-Naturw. Klasse IIa,* **139** (1930) Heft 7–8.
F. URBACH–G. SCHWARZ, *ibid.,* **139** (1930) 483.
F. G. WICK, *J. Opt. Soc. Am.,* **21** (1931) 223.
J. T. RANDALL–M. H. F. WILKINS, *Proc. Roy. Soc. London,* **A184** (1945) 366.

TABLE II

Base Material	Activator	Additional activator (sensitizer)	References
oxides and sulphides of alkaline earth metals	*Sm, Pr, Nd*	*Bi, Pb*	1
$CaWO_4$	*Sm*	*Pb*	2, 3
$(Cd\text{–}Be)WO_4$	*Sm*	*Bi*	4
$(Ca\text{–}Cd)MoO_4$	*Sm*	*Pb*	5
tungstates and molybdates	*Sm*	*Pb, Bi, Ag, Cu*	6
Glass	*Dy*	*Ce*	7
Zinc borate glass	*Mn*	*Ce*	8
Zinc alumo-phosphate glass	*Mn*	*Sn*	9
Phosphate glass	*Mn*	*Ce, Sn*	10, 11
Ca, Sr, Ba, Mg phosphate	*Mn*	*Ce*	12
Silicates	*Mn*	*Ce*	13, 14
$CaSiO_3$	*Mn*	*Pb*	15
Phosphates, borates Silico-phosphates Silico-borates	*Mn*	*Ag, Tl, Sn, Pb, Ce, Sb*	16
$Ca_2P_2O_7$	*Mn*	*Sn, Sb, Sm*	17
$Cd_5ClP_3O_{12}$	*Mn*	*Sb*	18
$A_5XP_3O_{12}$ ($A = Ca, Sr$; $X = F, Cl, Br$)	*Mn*	*Sb, Bi, Sn, Pb*	19, 20
$SrZrO_3$	*Bi*	*Pb*	21
$NaCl$	*Mn*	*Pb*	22
$CaCO_3$	*Mn*	*Pb, Tl, Ce*	23

1. S. ROTHSCHILD, *Naturw.*, **20** (1932) 850; *Phys. Z.*, **35** (1934) 557; **37** (1936) 757.
2. F. SWINDELLS, *J. Opt. Soc. Am.*, **23** (1933) 129.
3. N. RIEHL, *Phys. u. techn. Anw. Lum.*, Berlin 1941, p. 96.
4. H. M. FERNBERGER, U.S.A. Pat. Spec. 2.361.467.
5. H. C. FROELICH–A. R. HERSEY, Brit. Pat. Spec. 577.302,
6. U.S.A. Pat. Spec., 2.258.472.
7. P. PRINGSHEIM–S. SCHLIVITCH, *Z. Phys.*, **61** (1930) 305.
8. B. E. COHN–W. D. HARKINS, *J. Am. Chem. Soc.*, **52** (1930) 5146.
9. J. G. HOOLEY, U.S.A. Pat. Spec. 2.400.147.
10. M. HÜNIGER–H. PANKE, U.S.A. Pat. Spec. 2.284.055.
11. Brit. Pat. Spec. 476.945.
12. H. C. FROELICH, U.S.A. Pat. Applic. Serial Nr 498.731.
13. B. E. COHN–W. D. HARKINS–G. ASCHERMANN, D.R. Pat., 715.722.
14. G. ASCHERMANN–H. STRÜBIG, U.S.A. Pat. Spec. 2.308.736.
15. H. C. FROELICH, Brit. Pat. Spec., 577.694.

16. M. HÜNIGER–H. PANKE, Brit. Pat. Spec. 512.154; U.S.A. Pat. Spec. 2.241.950, 2.241.951, 2.270.124.
17. A. H. McKEAG–P. W. RANBY, Brit. Pat. Spec. 578.272.
18. Brit. Pat. Spec. 577.089.
19. A. H. McKEAG–P. W. RANBY, Brit. Pat. Spec. 578.192; 578.195. *The Industrial Chemist* (1947) 597.
20. H. C. FROELICH, U.S.A. Pat. Applic. Serial Nr 592.277.
21. H. C. FROELICH, U.S.A. Pat. Applic. Serial Nr 469.467.
22. K. J. MURATA–R. L. SMITH, *Am. Mineralogist*, **31** (1946) 527.
23. J. H. SCHULMAN–L. W. EVANS–R. J. GINTHER–K. J. MURATA, *J. Appl. Phys.*, **12** (1947) 732.

are superposed, the various emissions will occur simultaneously. If there is no transfer of energy between the different mechanisms, the relative intensity of the different emission bands is determined by the ratio of the absorption coefficients and the efficiency of the luminescence processes. If a transfer of energy occurs between the various mechanisms, however, the relative intensity of the emission bands is not solely determined by the two factors mentioned, but also by the relative magnitude of the transition probabilities for the various emissions, together with the probability of the energy transfer itself. Due to these factors it may happen that an emission corresponding to a strong absorption band, is completely quenched by an emission corresponding to a much fainter absorption.

Mg_2TiO_4–Mn is an example of a system in which energy transfer does not occur. Examples of cases in which transfer of energy occurs are provided by the system anthracene-naphtacene [1] and $CaWO_4$–Sm (Cf. Chapter III, Section 8). The zinc-sulphide luminophors also belong to this type, an extremely small amount of activator suppressing the fundamental emission of the matrix lattice at —180° C [2], while also radiation absorbed in the absorption band of one activator may be emitted in the emission band of another activator [3].

[1] E. J. BOWEN, Nature, **153** (1944) 653; *J. Chem. Phys.*, **13** (1945) 306.
[2] F. A. KRÖGER, Physica, **7** (1940) 1.
[3] H. A. KLASENS, Nature, **158** (1946) 306.
M. SCHÖN, *Z. Phys.*, **119** (1942) 463; *Forsch. u. Fortschritte*, **19** (1943) Nr 23/24.

12. SENSITIZATION

The fact that an emission may be excited by absorption in a band which does not correspond to it may be used when we wish to make a certain luminophor excitable in a wavelength region in which it normally does not absorb. This is called sensitization [1]. An absorption in the particular region may be introduced by incorporating foreign ions, or in one of the other ways in which additional energy levels may be made to occur (cf. Sections 5 and 6). The purest case of sensitization is that in which the emission corresponding to the new absorption does not occur, all energy being transferred to the original activator. This is realized in *CaO–Sm*, sensitized by lead (ref. 1 of Table II). In all the other cases of sensitization of luminescence known hitherto, however, the energy is only partly transferred. The sensitizer functions as an activator itself and only quantitative investigations show that we are actually dealing with a case of sensitization and not simply with double activation. Table II shows a survey of the sensitized systems known.

Incidentally it may be emphasized that sensitization is not exclusively connected with luminescence, but occurs also in various photo-chemical processes. Thus the formation of a latent image in silver halides upon irradiation with a wavelength which is not absorbed in these halides becomes possible when certain organic dyes are adsorbed at the crystal surface (photographic sensitization). On the other hand certain organic substances become succeptible to the action of a radiation by which they are normally inaffected, when they are adsorbed at solids absorbing this particular radiation [2].

[1] This sensitization must not be confused with sensitization of luminophors for infra red. The sensitization considered in this section consists in the causing of a new absorption band, absorption into which leads to excitation. Sensitization for infra red causes an absorption for infra red which effects the release of energy stored after normal excitation.

[2] C. F. Goodeve–J. A. Kitchener, *Trans. Far. Soc.*, **34** (1938) 902.
C. Cohn–C. F. Goodeve, *Trans. Far. Soc.*, **36** (1940) 433.

These different kinds of sensitization may probably be considered from one point of view, energy transfer and energy transport being the essential processes in all of them.

13. ENERGY TRANSFER AND ENERGY TRANSPORT

When a certain emission is excited by absorption in a band which does not correspond to it, each being related to a different electronic transition, energy absorbed in one mechanism must necessarily be transferred to the other mechanism. Let us consider first a situation in which both processes occur at the same or nearly the same position in the lattice. Transfer of excitation energy may then occur in one of the following ways:

1. The initial absorption is first followed by the emission corresponding to it; this emission is reabsorbed in an absorption band of the other centre and thus causes emission in this centre.
2. The excited state primarily formed is transformed in a single quantum-mechanical resonance process into an excited state of the other kind without any intermediate radiation, the excess of energy being lost as heat.
3. When the absorption process has liberated electrons from their holes, the holes primarily formed may be filled up with electrons from other ions whose occupied states lie above the starting level of the absorption process (cf. Fig. 5B, II). The new emission results when the excited electrons finally recombine with the holes in their new hosts. It may also happen that not the holes, but the excited electrons temporarily occupy an intermediate state (cf. Fig. 5B, I): the liberated electrons fall to unoccupied activator states below the primary excitation level, and return to their initial ground state with the emission of a new band. The energy liberated on the trapping of the hole or the electron in the intermediate state may be emitted as radiation (infra red) or may be dissipated as heat [1].

In a number of cases it is evident that absorption and the

[1] M. Schön, Z. Phys., **119** (1942) 463; *Forsch. u. Fortschritte*, **19** (1943) No 23/24.

emission caused by it do not occur at the same points in the lattice. For instance in activated crystals in which excitation in the absorption band of the matrix lattice causes emissions associated with the activator, the absorption certainly occurs all over the matrix lattice, while the luminescence transitions occur exclusively in or near the few activators. In these cases energy transfer requires a transport of the energy through the lattice over a considerable distance. The four transfer processes discussed above each suggest a transport mechanism:

1′ Selfabsorption is not restricted to adjacent points, but may also occur over larger distances.

2′ The resonance process will especially occur with excitons. These excitons may travel as such through the lattice (cf. Section 3.2).

3′ The excitation energy may be carried through the lattice by excited electrons and holes moving independently.

Although energy transfer and energy transport may well take place according to the same mechanism, this is not essential. It might be, for instance, that energy would be transported by separate electrons and holes, but would finally be transferred to the centre by a resonance process. Selfabsorption occurs in a great many cases, but it is probably not responsible for the most outstanding cases of energy transfer in which in spite of an extremely low activator concentration, emissions associated with a strong initial absorption are completely suppressed. The mechanisms 2 and 2′ are probably realized in *$CaWO_4$-Sm* (Chapter VI, Section 4.4), while the mechanisms 3 and 3′ are now accepted for zincsulphide luminophors in which photo-conductivity and a hyperbolic decay law point to the separation of electrons and holes in the absorption process and their recombination during the emission. These questions will be treated more in detail in the consideration of temperature dependent processes (Chapter VI).

Transport of energy, discussed here with regard to the phenomenon of luminescence, probably occurs in a large number of other cases. In general it will occur when energy absorbed at one point, gives rise to effects of some kind in another point some distance away; sensitized photo-chemical

reactions (cf. Section 8), but also biological processes. The migration of energy is one of the important problems in physics to-day [1].

14. CLASSIFICATION OF KNOWN LUMINESCENT EFFECTS.

It has been shown in the preceding sections that it is possible to distinguish between transfer processes and characteristic processes. Now we shall try to classify the known luminescent effects according to this distinction.

A fundamental or lattice emission of pure crystals has been observed up till now at low temperatures with *ZnS*, *ZnO*, *CdS* [2] and with *NaCl*, *KCl*, *NaBr* and *KBr* [3]; in all these cases the emission was situated immediately against the long wave-length edge of the absorption [4]. Ultra violet emissions observed with Al_2O_3, Be_2SiO_4 and β-Zn_2SiO_4 may also be of this type [5]. Further investigations at low temperatures will probably reveal that all simple compounds are capable of showing an emission of the same type. Because of their position on the wave-length scale next to the absorption edge, for various substances these emissions will fall in the region of vacuum spectrography.

Emissions of perturbed crystals are known for a number of partly decomposed compounds [6] and for diamond [7], and also

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[1] N. RIEHL, Naturw., **28** (1940) 601; *Phys. u. techn. Anw. der Luminescenz*, Berlin 1941, p. 57.
J. FRANCK–E. TELLER, *J. Chem. Phys.*, **6** (1938) 861.

[2] F. A. KRÖGER, *Physica*, **7** (1940) 1.

[3] W. KUDRIAVZEWA, *Z. Phys.*, **90** (1934) 489.
N. N. FEDENEW, *Acta Physicochim. U.R.S.S.*, **9** (1938) 905.

[4] In previous publications on purely empirical grounds we called an emission of this kind an "edge emission". A more suitable denomination seems to be "lattice emission" or "fundamental emission" in accordance with the corresponding terms proposed for the absorption.

[5] H. W. LEVERENZ, R.C.A. *Review*, **7** (1946) 205.

[6] A. KUTZELNIGG, *Z. anorg. allgem. Chem.*, **201** (1931) 323.
,, ,, *Monatsh. Chem.*, **61** (1932) 69.
,, ,, *Trans. Far. Soc.*, **35** (1939) 146.
J. EWLES, *Trans. Far. Soc.*, **35** (1939) 119.
W. BYLER, *J. Am. Chem. Soc.*, **60** (1938) 1247.
H. GOBRECHT, *D.R. Pat.* 718.338.

for substances showing deviations from the stoechiometric composition such as *ZnO* [1,2,3] *ZnS* [3,4] and alkali halides containing F-centra [5] probably belong to the transfer type.

As it is our opinion that in very many cases the luminescence of activated luminophors is of the characteristic type, it seemed worth while to assemble data concerning activated luminophors, and to arrange them according to the activators.

Table III (p. 262) gives for each activator its luminescence effects in various matrix lattices.

The number in the column "references" point to the references underneath each table. The famous handbook article by LENARD, SCHMIDT and TOMASCHEK (Handbuch Exp. Physik XXIII/I (1928) is quoted as LST followed by the page in question.

Those luminophors in which, according to the literature, luminescence is caused by activation due to a particular ion but in which later investigations have proved it to play no essential part (e.g., *Ag* in $CaWO_4$–*Ag*) have not been included. Luminophors in which in one matrix lattice a certain emission is stimulated by a number of different activators, and where probably secondary activation occurs (e.g., the ultra-violet emission in *CaO*, *CaS*, etc., stimulated by *Fe*, *Bi*, a.o., the blue emission of *ZnS* stimulated by *Ag*, *Zn*, etc.) have been included but the emissions concerned have been placed between brackets.

In Table IV we give for each activator a summary of all luminescence effects connected with it and the type to which they probably belong, *C* referring to the characteristic ionic type, *T* to the transfer type. For the characteristic emissions

D. H. KABAKJIAN, *Phys. Rev.*, **57** (1940) 700.
H. S. TASKER–F. F. RENWICK, *U.S.A. Pat. Spec.* 2.336.815; 2.289.384; 2.289.997.
[7] C. V. RAMAN, *Proc. Indian Acad. Sci.*, **19A** (1944) **199**.
[1] E. KÖRNER, *Dissertation* Greifswald, 1930.
[2] E. BEUTEL AND A. KUTZELNIGG, *Sitz. Ber. Ak. Wien*, IIa, **141** (1933) 437.
[3] SCHAEFERS, *Dipl. Arbeit techn. Hochschule*, Berlin, 1938.
[4] J. GLASSNER, *Dissertation*, Berlin, 1938.
[5] M. DJACHENKO–W. SELEGENEW, *J. Exp. Theoret. Phys.* (russ), **11** (1941) 530.

TABLE IV

Activ- ator	Colour of the lum.	Type of lum.	Responsible atom/ion/complex
Ag	white	*C*	*Ag*
	blue, green, yellow	*C* ?	?
As	green	?	—
Au	?	?	—
Bi	blue, green, red	*C* ?	Bi^{3+}
C	white	*T*	—
Cd	blue, yellow	*T* ?	—
Co	green; yellow; orange	*C* ?	Co^{2+} ?
Cr	red	*C*	Cr^{3+}
Cu	red + blue	*C*	*Cu*
	violet, blue	*C* ?	?
	blue, green, red	*T*	—
Fe	blue?; red	*T*?; *C*	Fe^{2+}?
Ga	red ?	?	—
Hg	yellow, red	*C*	?
Mn	green, yellow, red	*C*	Mn^{2+}
	red	*C*	Mn^{4+}
Mo	(violet, blue) green, yellow	*C*	MoO_4^{2-}
Nb	?	?	
Ni	red, infra red	*C*	Ni^{2+}
Pb	blue, green, yellow, red	*C*	Pb^{2+} or $(Pb^{2+}X_n)^{m-}$
Pt	green, yellow	*C*	$[Pt(CN)_4]^{2-}$
Re	yellow, pink	*C*	Re^{2+} ?
Rh	red	*C*	Rh^{3+}
Sb	yellow, blue	*C*	Sb^{3+}
Si	blue, yell. red	*T* ?	
Sn	blue, green, yellow	*C*	$(Sn^{2+}X_n)^{m-}$
Ta	?	?	
Th	blue	*C* ?	
Ti	blue + green; yellow	*C*	$(Ti^{4+}X_n)^{m-}$
Tl	violet	*C*	Tl^{+}
	blue, green, yellow	*C*	$(Tl^{+}X_n)^{m-}$
U	green, yellow	*C*	UO_2^{2+}
	yellow, red	*C*	UO_4^{2-}
V	green, yellow, red	*C*	VO_4^{3-}
W	violet, blue, green	*C*	WO_4^{2-}
Zn	blue, green, red	*T*	
Zr	blue (*Ti* ?)	*C* ?	
Rare Earths			
Ce	ultra violet, blue	*C*	Ce^{3+}
	green, red	*C* ?	$(Ce^{4+}O_x)$
Dy	blue–red	*C*	Dy^{3+}
Er	green	*C*	Er^{3+}

TABEL IV (continued)

Activator	Colour of the lum.	Type of lum.	Responsible atom/ion/complex
Rare Earths			
Eu	orange	*C*	Eu^{3+}
	blue	*C*	Eu^{2+}
Gd	ultra violet	*C*	Gd^{3+}
Nd	green + infra red	*C*	Nd^{3+}
Pr	green + red	*C*	Pr^{3+}
Sm	orange	*C*	Sm^{3+}
	red	*C*	Sm^{2+}
Tb	u. v.–red	*C*	Tb^{3+}
Tu	u. v. + blue + red + infra red	*C*	Tu^{3+}
	red	*C*	Tu^{2+}
Yb	yellowish green	*C*	Yb^{2+}
	?	*C*	Yb^{3+}

C = luminescence characteristic of an ion or complex.
T = transfer luminescence.

the ions which are supposed to play a part are given in the fourth column. The symbol *X* is used in complex ions to represent different constituent ions such as *O*, *S*, halides, etc. The emissions placed between brackets in Table III, which must be assumed to be caused by secondary activation, are not included in Table IV. To do so would be of little value, as in principle every element is able to cause secondary activation: whether it actually occurs or not does not depend solely on the activator but also on the matrix lattice in which it is built in.

For the classification we have already made use of the experimental results about which will be reported in the experimental part of this book.

The emission due to the rare earths, chromium, mercury, platinum, rhodium, antimony, uranium [1] and vanadium is so constant in the various matrix lattices that these emissions must belong to the characteristic type.

[1] It may be anticipated that plutonium, which is the third member of a new series of rare earths elements of which uranium is the first one, will cause characteristic luminescence effects resembling the ones found with uranium.

With manganese, titanium, tungsten and molybdenum colour differences occur: for manganese, for instance, the emission varies between green and red. Though this in itself is evidence in favour of the transfer type, yet absorption measurements show that these emissions must be attributed also to the characteristic type. In some cases, in spite of comparatively thorough investigations, the attribution remains extremely difficult. As an example we may describe the situation for thallium. In pure thallium halides, in solid solutions of these substances in alkali halides and in aqueous solutions containing in addition high concentrations of alkali halides nearly identical absorption bands were observed [1, 2, 3].

According to SEITZ [4] for the solid solutions these absorption bands must be attributed to electronic transitions within the thallium ion (Tl^{+}). FROMHERZ [2] however, drawing conclusions from his observations on aqueous solutions, assumes the bands to be characteristic of thallium-halide complexes. Eventually the great resemblance with the fundamental absorption of the alkali halides suggests that we might have to deal with an absorption of the fundamental type (transfer of an electron from the negative ions to the thallium). We personally are inclined to believe, that the situation may be satisfactorily described by means of a complex, the optical properties of which are mainly determined by the central ion [5]; a model which differs only slightly from the ionic hypothesis. The same probably applies to the absorption and emission of alkali halides containing tin [6], lead, copper and silver [2, 7].

In contrast to this the well known emissions connected with copper and silver in zinc sulphide undoubtedly belong to the transfer type. There is no need to be disturbed by this

[1] R. HILSCH–R. W. POHL, *Z. Phys.*, **48** (1928) 384.
[2] H. FROMHERZ, *Z. Phys.*, **68** (1931) 233.
[3] P. PRINGSHEIM, *Rev. Modern Phys.*, **14** (1942) 132.
[4] F. SEITZ, *J. Chem. Phys.*, **6** (1938) 150.
[5] Compare the complex ions existing in chromates, manganates, etc.
[6] M. HÜNIGER–J. RUDOLPH, *Z. Phys.*, **117** (1940) 81.
[7] R. HILSCH, *Phys. Z.*, **38** (1937) 1031.
H. FROMHERZ–W. MENSCHICK, *Z. phys. Chem.*, (B) **3** (1929) 1.

apparent contradiction: in principle one activator may very well give rise to emissions of different types, especially when it causes secondary activation and perturbations of the lattice as is probably the case with silver in zinc sulphide. Despite the great number of investigations concerning the green luminescence of *ZnS–Cu* it cannot yet be stated whether the copper itself provides the level involved in the luminescence transition (direct activation) or whether the level belongs to one of the ions of the lattice, perturbed by the presence of the copper (indirect activation).

For arsenic, bismuth, cadmium, gallium, iron, nickel, cobalt, silicon, thorium and zirconium the data available are insufficient to draw definite conclusions. When taking into account the close chemical relationship between manganese and chromium on one side, and iron, nickel and cobalt on the other, we expect that the latter may also be able to cause an emission of the characteristic type, possibly in the infra red.

The emissions connected with carbon and silicon, the emissions of Be_3N_2 containing AlN [1] and of inorganic substances containing organic anions [2] presumably belong to the electron transfer type.

An ultra violet luminescence, observed with $NaCl$ containing hydrogen [3], may correspond to the *U*-absorption band. According to the picture usually accepted for this absorption [4], the emission would be of the transfer type.

Although organic substances have not been considered up till now, it may be emphasized that absorption and emission in these substances are usually of the characteristic type, the processes being characteristic of the molecules or even of a part of the molecules from which the crystals are built up

[1] S. SATOH, *Nature*, **133** (1934) 837; *Sc. Pap. Inst. Phys. Chem. Res. Japan*, **29** (1936) 41.
[2] J. GLASSER–R. P. FONDA, *J. Am. Chem. Soc.*, **60** (1938) 722. W. BYLER, *J. Am. Chem. Soc.*, **60** (1938) 1247.
[3] N. N. FEDENEW, *Acta Physicochim. U.R.S.S.*, **9** (1938) 905.
[4] R. W. POHL, *Proc. Phys. Soc.*, **49** (suppl.) (1937) 1.

15. THE POSSIBILITY OF PREDICTION OF LUMINESCENCE FOR NEW SYSTEMS

Recently LEVERENZ posed the question whether it would be possible to predict the colour of the luminescence for a system never synthesized before [1]. Considering the effects of activators and lattice distortions in zinc sulphide and oxide and in the zinc silicates, the question had to be answered in the negative: Instead of by a well planned systematical research, new luminophors with a certain desired emission can only be obtained by carrying out a huge number of preparations "guided by scientific intuition rather than by logic". And further: "it is unwise to predict the colour (of the luminescence) of new compounds according to any preconceived notion of how the elements of the periodic table are combined in the phosphors".

We are not so pessimistic on this point. As far as the colour of luminescence is concerned, a considerable number of activators enable us to score certain hits. When properly incorporated in a suitable base material — a matter which is governed by such comparatively simple quantities as ionic radius and valency and which does not offer insurmountable difficulties — the rare earths (except cerium), chromium, tetravalent manganese (cf. Chapter II), mercury, uranium (uranyl and uranate, cf. Chapter IV) and the platinum cyanides will give rise to well defined, predictable emissions. The emissions caused by tungstate, molybdate, titanate, vanadate and stannate groups, and those due to divalent manganese, trivalent cerium, antimony, and complexes of lead, thallium and tin are somewhat more dependent on the surroundings, but even in these cases some prediction may be made. The emission of divalent manganese, for instance, is found somewhere between green and red: a blue emission will certainly never be caused by these ions. In the same way the emission of trivalent cerium occurs between 2600 and 5000 Å without exception.

One reservation must be made: the prediction may only

[1] H. W. LEVERENZ, *Proc. I.R.E.*, **38** (1944) 256; *J. Opt. Soc. Am.*, **32** (1942) 630.

be expected to come true if we do not get entangled in the numerous possibilities of transfer emissions, either involving secundary activation or not. As far as we found, however, this reservation has no very serious effects and is only of great importance with the sulphides. Far more difficulties arise when we wish to predict whether an emission will actually occur or not. Or, to put it more generally, what will be the intensity of the emission.

Generally speaking the intensity is determined by four factors:
1. the absorption of excitation energy
2. the transfer of the absorbed energy to the centres
3. the efficiency of conversion of excitation energy into luminescence in the centre
4. the absorption of the emission, generated in the centres, on its way out of the crystal.

Of these four factors the first and the fourth one may be provided for by choosing base materials which show absorption in the region in which we wish to excite, but not in the region in which we wish the emission to occur. The transfer of energy, however, is very difficult to predict and also the net efficiency of the centre offers serious difficulties: The energy of luminescence in the centre is mainly determined by temperature quenching, a problem which, as we shall see in Chapter VI, is still far from being solved.

Summarizing we can state that for characteristic activation the colour of the emission can be predicted exactly in some cases, more or less roughly in other cases, while for transfer emissions no prediction whatsoever can be made. In all cases the intensity of luminescence is still mainly a matter of chance.

II. MANGANESE AS AN ACTIVATOR

1. ON THE VALENCY OF MANGANESE AS AN ACTIVATOR

As is evident from Table III, List 13, manganese acts as an activator in a considerable number of substances. It is important to ascertain the valency states of the manganese responsible for the different emissions. In the early stages of research on luminescence, soon after the discovery of manganese as an activator in luminescent solids, LECOQ DE BOISBAUDRAN [1] was already occupied with this question. To this end luminophors prepared by heating either in an oxidizing or in a reducing atmosphere were compared as to the colour of the crystals and the intensity and colour of the luminescence. For Al_2O_3 and $CaCO_3$ [2] it was found that heating in a reducing atmosphere gave white products, showing intense green and orange luminescences respectively. The products heated in an oxidizing atmosphere showed a fainter luminescence. Besides under these circumstances the calcium carbonate was coloured coffee brown. Hence it was concluded that the manganese acting as an activator must be in the divalent state. The results more recently obtained by NICHOLS and WICK [3] pointed in the same direction: the intensity of the luminescence of calcium sulphate, calcium phosphate or calcium carbonate, each containing manganese as an activator was diminished by treatment with ozone.

According to BRÜNINGHAUS [4] the luminescent effects of various colours must be correlated with manganese in different valency states. Rightly supposing that a close relationship

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[1] LECOQ DE BOISBAUDRAN, *C.R.* Paris, **103** (1886) 468, 1067, 1107; **104** (1887) 330, 1680; **105** (1887) 261.

[2] LECOQ DE BOISBAUDRAN, *C.R.* Paris, **105** (1887) 1228.

[3] E. L. NICHOLS–F. G. WICK, *Proc. Nat. Ac. Sc.*, Washington, **16** (1930) 32.

[4] L. BRÜNINGHAUS, *Ann. Chim. Phys.*, (8), **21** (1910) 210.

must be expected between the absorption spectrum (defining the colour of the substance) and the emission spectrum, and starting from the experimental facts that the oxide of divalent manganese is green and the oxides of manganese of a higher valency are brown or red, BRÜNINGHAUS correlated the green luminescence with divalent manganese and the red or orange emission with manganese of a higher valency. The relation mentioned between the valency of the manganese and the colour of the manganese compound — though actually existing for the oxides — does not hold for other compounds: there are red manganous compounds (e.g., $MnSO_4$, $MnSiO_3$) and green manganic salts (e.g., $MnPO_4$). Hence, instead of proving a relation between the valency of the manganese and the colour of the luminescence, BRÜNINGHAUS' arguments make it probable that in principle manganese ions in each state may cause a luminescence of different colours.

For divalent manganese this could in fact be shown: Emissions varying from green to red are found with luminophors for which the presence and the activity of divalent manganese could be proved both by chemical and by physical methods; the latter being based on the spectra of absorption and excitation [1] (cf. Section 5 of this Chapter): $ZnSO_4$–$MnSO_4$, CdI_2–$MnCl_2$, $MnSiO_3$ are luminescent in a red colour, $CdSiO_3$–$MnSiO_3$ shows luminescence in an orange band, Zn_2SiO_4–Mn_2SiO_4 and $ZnAl_2O_4$ in a green band whereas $(Zn–Be–Mn)_2SiO_4$ shows luminescence effects from green to red, dependent on the composition.

Yet, it may not be concluded from this that manganese acting as an activator is divalent in *all* luminophors. Actually we found indications for the activity of manganese of a higher valency in a publication by TIEDE and VILLAIN [2] concerning magnesium orthotitanate activated by manganese.

With this substance these authors observed an obvious influence of the atmosphere of preparation upon the luminescense. We have repeated and extended their experiments

[1] F. A. KRÖGER, *Physica*, **6** (1939) 764; *Dissertation*, Amsterdam 1940, p. 17.
[2] E. TIEDE–E. VILLAIN, *Ber. d. chem. Ges.*, **73** (1940) 274.

with this system, and our results will be reported fully in Section 2 of this chapter. In addition however, they offered a motive to extend the experiments to other luminophors.

To this end we prepared a number of manganese luminophors in the usual way by heating a mixture of oxides or of compounds which easily decompose to oxides in a suitable proportion to give the desired substance, at a temperature high enough to guarantee a rapid reaction between the components but without the occurrence of melting. For each luminophor one sample was prepared in an oxidizing atmosphere (air or oxygen) and one in a reducing atmosphere (hydrogen or a mixture of nitrogen and hydrogen). In some cases where heating in these atmospheres was unsatisfactory we used a neutral atmosphere (nitrogen).

In Table V we give a list of the substances investigated, together with the manganese content in mol. percents, the temperature of preparation, the colour of the products and the colour and the intensity of the luminescence produced by cathodic bombardment.

With $MgSiO_3$, $Mg_3(PO_4)_2$, $Mg_2P_2O_7$, $MgSO_4$, MgO, ZnB_2O_4, $Zn_3B_2O_6$, $CaCO_3$, $Ca_2B_2O_5$ and CaB_2O_4 no essential dependence of the luminescence on the atmosphere of heating could be detected. In some cases the luminescence of the reduced products was slightly diminished by a greyish colouring of these substances, probably due to small amounts of carbon from decomposed organic contaminations. The blue emission occurring with $Mg_2P_2O_7$–Mn next to the orange-yellow manganese emission could also be found with the phosphates not containing manganese, when heated under the same conditions: the effect is hence certainly not correlated with manganese, but must be due either to some unknown activator or to the phosphate itself (partial decomposition?). The luminescence of the borates of calcium and zinc[1] which is different for products of various compositions (nrs 6, 7, 20 and 21 in Table V) deserves particular attention: Both

[1] For the zinc borates our results are in accordance with observations by H. FRIEDRICH, *Dissertation* Jena, 1938 and J. W. STRANGE, *Brit. Pat. Spec.* 410.159, *Fr. pat.* 770.728.

TABLE V

No.	Matrix substance	*Mn*-content in at. *Mn*/mol	Heating temp. °C	Colour of the product			Colour and intensity of the cathodo-luminescence						Remarks
				oxid. atm.	neutr. atm.	red. atm.	oxid. atm.		neutral atm.		red. atm.		
1	α-Al_2O_3	2×10^{-3}	1500°	purple		white	red	*f*			—		
2	$CaO.6Al_2O_3$	1×10^{-3}	1500°	rose		white	red, green	*m*			green	*s*	$= \beta$-Al_2O_3
3	$SrO.6Al_2O_3$	,,	1500°	rose		white	red, green	*m*			green	*s*	$= \beta$-Al_2O_3
4	$BaO.6Al_2O_3$	,,	1500°	white		white	green	*s*			green	*s*	$= \beta$-Al_2O_3
5	$Na_2O.11Al_2O_3$	,,	1200°	rose		white	red, green	*m*			green	*s*	$= \beta$-Al_2O_3
6	$Ca_2B_2O_5$	2×10^{-2}	800°	rose		rose	orange	*s*			orange	*s*	
7	CaB_2O_4	1×10^{-2}	900°	rose		rose	green	*s*			green	*s*	
8	$CaCO_3$	,,	700°	white		white	orange	*s*			orange	*s*	
9	$Cd_3B_2O_6$	,,	800°	white	*x*	*x*	green		—		—		
10	$Cd_2B_2O_5$	,,	800°	rose	*x*	*x*	orange		—		—		
11	CdB_2O_4	,,	800°	white	*x*	*x*	green		—		—		
12	CdB_4O_7	,,	800°	white	*x*	*x*	green		—		—		
13	$MgSiO_3$	1×10^{-3}	1100°	white		greyish	red	*s*			red	*m*	
14	$Mg_3(PO_4)_2$	3×10^{-3}	1000°	white		greyish	orange	*s*			orange	*m*	reduced, unact
15	$Mg_2P_2O_7$	2×10^{-3}	1000°	white		white	orange-yellow	*s*			or. yell. +blue	*s*	$Mg_2P_2O_7$ fl. f. blue
16	$MgSO_4$	1×10^{-3}	1000°	rose		rose	orange	*s*			orange	*s*	
17	$MgAl_2O_4$	,,	1600°	yellow		white	green, red	*m*			green	*s*	
18	MgO	,,	1500°	greyish		white	orange	*m*			orange	*s*	
19	Mg_2TiO_4	2×10^{-3}	1300°	yellowish brown	grey	dark blue *x*	red	*m*			—		
20	$Zn_3B_2O_6$	3×10^{-2}	800°	white		greyish	orange	*s*			orange	*s*	
21	ZnB_2O_4	1×10^{-2}	700°	white		greyish	green	*s*			green	*s*	
22	$ZnSO_4$	,,	650°	white	white	dark brown *x*	red	*s*	red	*s*	—		
23	$ZnAl_2O_4$	,,	1400°	yellowish	white	*x*	green	*s*	green	*s*	—		

s = strong *m* = medium *f* = faint *x* = decomposed

BRÜNINGHAUS [1] and CURIE [2], relying on a reputed influence of the atmosphere of preparation, correlate the different colours with manganese in various valency states. While these authors came to exactly opposite conclusions, we were unable to observe anything like an influence of the atmosphere. Therefore it seems probable that the differences found by BRÜNINGHAUS and CURIE must not be attributed to different valency states of the manganese, but to differences in the crystal structure: crystalline products of different composition — but all containing divalent manganese — must have been formed under the influence of more or less haphazard circumstances.

The various crystalline phases in the system $CdO–B_2O_3$ (Nrs 9, 10, 11, 12) show similar differences in the colour of the luminescence. As a reducing and even a neutral atmosphere of preparation causes decomposition, indications of the valency of the manganese cannot be obtained by comparing the products made under oxidizing and reducing conditions. Therefore, we have determined by means of titration, whether the substances had any oxidizing power with respect to potassium iodide [3], as would be expected if manganese of a higher valency was present. The results were absolutely negative, proving that the manganese exists in the divalent state in all cadmium borates, the orange-luminescent $Cd_2B_2O_5–Mn$ included.

With $MgAl_2O_4$, Mg_2TiO_4, α-Al_2O_3, and the substances belonging to the β-Al_2O_3 group: $CaO.6Al_2O_3$, $SrO.6Al_2O_3$, and $Na_2O.11Al_2O_3$, the conditions of preparation very clearly affected the emission as well as the absorption of the powders, whereas for $ZnAl_2O_4$ an influence upon the absorption spectrum only could be detected.

As far as the absorption spectrum is concerned, the oxidized substances are more deeply coloured than the products heated in a non oxidizing atmosphere. As the unactivated substances

[1] L. BRÜNINGHAUS, *Ann. Chim. Phys.*, **20** (1910) 263; *J. Phys. Radium*, **12** (1931) 398.
[2] M. CURIE, *Trans. Far. Soc.*, **35** (1939) 116.
[3] The experimental procedure is described in section 2.3 of this chapter.

do not show this variation [1], the effect must be ascribed to an extra absorption band correlated with the manganese.

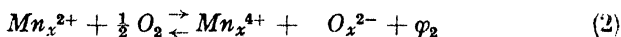
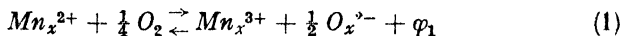
The emission data present the general aspect of green luminescence bands shown by the reduced products and red and green luminescence bands occurring with the oxidized products.

The phenomena of both absorption and emission justify the assumption that the green luminescence in the reduced products is due to divalent manganese, while the red luminescence and the extra absorption shown by the oxidized products are due to manganese of a higher valency. Anyhow we shall use this assumption as a working hypothesis for the description of the more precise experiments with some of the systems concerned, to be described in the following parts.

Our assumption finds its theoretical basis in the thermodynamics of homogeneous phases: in every homogeneous phase in which an ion may occur in various valency states, an equilibrium must exist between these states. The position of the equilibrium, determined by the thermodynamic potentials of the ions, depends on the nature of the crystalline or glassy matrix phase and on some variable factors such as the temperature and the oxidizing power of the surrounding gas atmosphere (e.g., the oxygen pressure).

The effects to be expected upon variations in the temperature or in the oxygen pressure may be shown by writing down the chemical equations connected with the oxidation and applying the laws of thermodynamics to them. In our case, in which we are probably concerned with the ions Mn^{2+}, Mn^{3+} and Mn^{4+} these equations are

$$Mn_x^{2+} + \tfrac{1}{4}\,O_2 \rightleftarrows Mn_x^{3+} + \tfrac{1}{2}\,O_x^{2-} + \varphi_1 \qquad (1)$$

$$Mn_x^{2+} + \tfrac{1}{2}\,O_2 \rightleftarrows Mn_x^{4+} + \quad O_x^{2-} + \varphi_2 \qquad (2)$$

The suffix x here indicates that we are not dealing with the free ions, but with the ions embedded in the crystal lattice.

[1] Mg_2TiO_4 is decomposed to a dark blue substance by heating in a reducing atmosphere. Heated in nitrogen, however, it remains perfectly white.

φ_1 and φ_2 are the heat effects involved in the oxidation. According to thermodynamics for the first reaction the equilibrium is given by the expression

$$\ln \frac{C_{Mn_x^{3+}} \cdot C_{O_x}^{\frac{1}{2}}}{C_{Mn_x^{2+}} \cdot C_{O_2}^{\frac{1}{4}}} = \frac{\varphi_1}{RT} + \text{constant}_1$$

Assuming that the concentration of O^{2-} in the phase is so high, that a slight variation may be neglected, $C_{O_x}{}^{2-}$ becomes a constant. Assembling the constants we get:

$$\ln \frac{C_{Mn_x^{3+}}}{C_{Mn_x^{2+}}} - \tfrac{1}{4} \ln C_{O_2} = \frac{\varphi_1}{RT} + \text{const}_1' \qquad (3)$$

and analogously for (2):

$$\ln \frac{C_{Mn_x^{4+}}}{C_{Mn_x^{2+}}} - \tfrac{1}{2} \ln C_{O_2} = \frac{\varphi_2}{RT} + \text{const}_2' \qquad (4)$$

Neglecting the entropy effects given by the constants which are relatively small under these circumstances, the whole situation is determined by the heat effects φ_1 and φ_2.

When these effects are strongly negative, which may occur when the insertion of Mn^{3+} or Mn^{4+} costs far more energy than that of Mn^{2+}, then Mn^{3+} and Mn^{4+} do not occur to an appreciable extent, whatever the other conditions may be. This might be the reason for the fact that in most luminophors the manganese is only present in the divalent state. (A second possible reason is given in Section 2.2.). When the heat effects are positive a co-existence of Mn^{2+}, Mn^{3+} and Mn^{4+} may occur. Depending on the magnitude of φ_1 and φ_2, on the oxygen pressure and on the temperature, the relative concentrations vary. As special cases it may be realized that two valency states co-exist in measurable concentrations together with a negligible amount of the third one [1].

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[1] This case seems to be realized with Mn_3O_4, Mn_2O_3 and in

An increase of temperature shifts the equilibrium in the direction of the lower valencies (dissociation of MnO_2 or Mn_2O_3 to MnO) whereas under all circumstances (i.e., even for negative heat effects) a high oxygen pressure favours the existence of the higher valency states.

Observations on glasses containing *Cr, Fe, Mn,* and *U* [1] which are also homogeneous phases and hence theoretically entirely equivalent with our cases, are in perfect accordance with these deductions. In the following we shall see whether our picture and its consequences can be applied to the luminophors whose properties are dependent on the composition of the gas atmosphere in which they have been prepared.

2. MAGNESIUM ORTHOTITANATE ACTIVATED BY MANGANESE

2.1. Introduction

In the pure state magnesium orthotitanate is practically non luminescent at room temperature. According to TIEDE and VILLAIN [1] on the introduction of small quantities of manganese a product can be obtained which shows a red luminescence ($\lambda_{max} = 6550$ Å) when excited by ultra violet radiation of a wave-length between 3100 and 4000 Å. For the preparation two points proved to be of particular interest, viz., the atmosphere in which the products were fired and the rate of cooling after the heating. When heated in a neutral atmosphere (N_2), the colour of the products was greenish white and the substances did not show any luminescence. Firing in an oxidizing atmosphere gave yellowish white substances, showing the red photoluminescence. In the latter cases

solid solutions of Mn_3O_4 in Fe_2O_3 in which a coexistence of Mn^{2+} and Mn^{4+} is assumed.

E. J. W. VERWEY–M. G. v. BRUGGEN, *Z. Kristallogr.*, **92** (1935) 136.

E. J. W. VERWEY–J. H. DE BOER, *Rec. Trav. chim.* P.B., **55** (1936) 531.

A. E. VAN ARKEL–E. J. W. VERWEY–M. G. v. BRUGGEN, *Rec. Trav. chim.* P.B., **55** (1936) 331.

[1] C. KÜHL–H. RUDOW–W. WEYL, *Sprechsaal,* **71** (1938) 91, 104, 117.

[1] E. TIEDE–E. VILLAIN, *Ber. d. chem. Ges.*, **73** (1940) 274.

the intensity of the luminescence was high for products cooled slowly from the heating temperature (1300° C) to room temperature, while rapid cooling gave products showing only an extremely faint luminescence effect. The necessity of firing in an oxidizing atmosphere was also mentioned by KRAUTZ [1]. Though not being conscious of the presence of manganese in his powders, this author observed a red luminescence with Mg_2TiO_4 when fired under oxidizing circumstances, which emission was completely destroyed by a treatment in hydrogen.

As we have already seen in the previous section the results of our own preliminary experiments are in accordance with these observations. In the following we will describe a more thorough investigation.

2.2. Preparation

2.2.1. *Formation of the titanate*

Mg_2TiO_4–Mn was prepared by heating MgO, TiO_2 and MnO in a very fine and reactive state as obtained by precipitation from solutions, at a temperature above 1200°, preferably at 1300° C. The magnesium and manganese were used in the form of highly purified acetates or chlorides. For titanium we started from titanium tetra chloride which could easily be purified by destillation. This liquid was poured into a 50% mixture of ethanol and water under rapid stirring and cooling with ice. Afterwards the sirup-like yellow liquid obtained was diluted with water to give a colourless easily flowing solution.

In order to obtain the reactive mixture of MgO, TiO_2 and MnO referred to above the solutions of Mg, Ti and Mn were mixed in the required proportion, then strong ammonia was added until complete precipitation occurred and finally the jelly-like mass was dried on a waterbath and fired at 500° C in air.

The molar ratio between MgO and TiO_2 leading to products showing an optimal luminescence must be two to one or higher. This proves that the active phase actually consists of Mg_2TiO_4.

[1] E. KRAUTZ, *Brit. Pat. Spec.* 487.520.

MgO present in excess above this composition is superfluous; it remains side by side with the Mg_2TiO_4, without doing much harm. At lower *MgO* contents $MgTiO_3$ occurs as a separate phase. As this metatitanate shows an absorption for 3650 Å, its presence is detrimental to luminescence.

2.2.2 *The essential phase of the preparation*

The Mg_2TiO_4–*Mn* formed by heating at 1300° C did not show any luminescence when formed in nitrogen, whereas the luminescence was faintly red for the products heated in an oxidizing atmosphere and cooled in the normal way by taking the sample out of the oven.
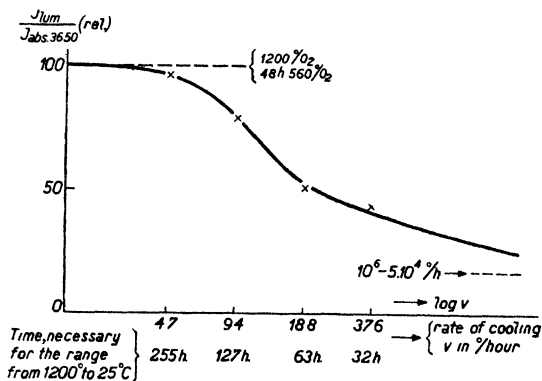
Fig. 6. Relative efficiency of the red luminescence of Mg_2TiO_4 — 0.002 *Mn* (excited by λ 3650 Å) as a function of the rate of cooling. The dotted line indicates the efficiency of an optimally annealed product.

With products containing 0.002 atoms manganese per mol Mg_2TiO_4 we have studied the way in which the rate of cooling affects the luminescence. As continuous cooling with an adjustable velocity was difficult to realize, we lowered the temperature discontinuously in steps of 25° C, keeping the samples at each temperature for a certain time. Fig. 6 gives the results showing that in accordance with TIEDE's observations slow cooling causes a strong luminescence.

Maximum intensities of luminescence are only reached when cooling rates of 4°/hour and lower are used and where accordingly the passage from 1200° C to room temperature takes at least 300 hours. Guided by our assumption concerning the various valency states of the manganese and the equilibria existing between them, we soon discovered that the slow cooling process, by which the sample passed successively through every temperature between 1200° C and 25° C, may be replaced by annealing at one temperature. Fig. 7 shows
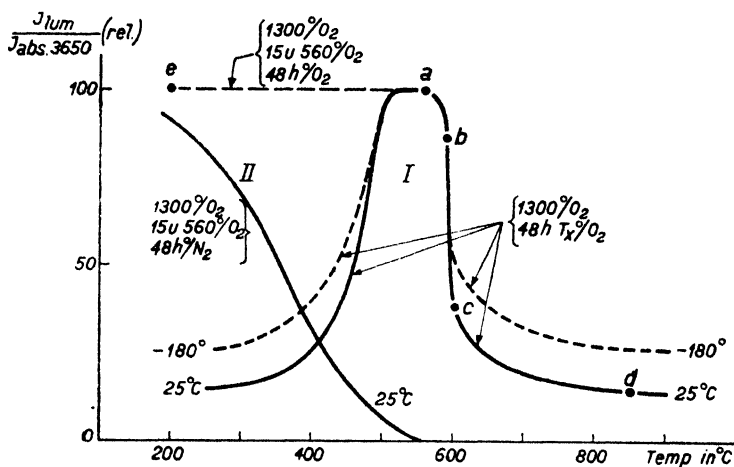
Fig. 7. Relative efficiency of the red luminescence of Mg_2TiO_4 — 0.002 Mn as a function of the annealing conditions:
I. oxidized, quenched products, afterwards annealed for 48 hours in oxygen; intensity measured at 25° C and −180° C.
II. Optimally annealed products, afterwards annealed for 48 hours in nitrogen.

the results, giving the intensity of the luminescence for products which were annealed for 48 hours in an atmosphere of pure oxygen. Above 600° C the annealing has no considerable effect, below 600° it increases rapidly, leading to maximum intensities between 500° and 560° C; below 500° C the effect decreases again. A prolongation of the annealing above 48 hours has no effect for temperatures above 500°: obviously

here an equilibrium state has been reached. Below this temperature, however, the luminescence increases slightly with prolonged heating and may finally reach the intensity of the products annealed between 500 and 460° C which correspond to the equilibrium state. Obviously the minimum time necessary to reach the equilibrium state is a function of temperature: at 600° about 8 hours are needed, at 560° C 15 hours, whereas at 450°, as we have seen, the stable state is not even reached in 48 hours.

The equilibrium state at low temperatures might be determined by using extremely long annealing times. We used a simpler method, starting from a maximally luminescent sample, made by annealing at 560° C. When annealed afterwards at a temperature between 300° and 500° it does not change its intensity of luminescence to the slightest extent indicating that the equilibrium state at these temperatures is identical with the one belonging to 560° C. Obviously this argument is only conclusive, if the oxidation is not completely frozen in at these temperatures. This is however not the case, as is shown by the reduction experiments described below.

In Fig. 7 the complete equilibrium state is given by the curve *e–a–b–c–d* [1].

The slowing down of the oxidation reaction in the low temperature region is also beautifully shown by the results of an investigation of the reverse process, the reduction. Optimally luminescent samples, made by annealing in oxygen at 560° C, were heated afterwards in an atmosphere of pure nitrogen. At 560° C the reduction occurs so rapidly that in 48 hours the luminescence is completely destroyed. Below this temperature the reaction is slower: from 450° C to 150° C an increasing part of the luminescence remains, while at still lower temperatures the luminescence is not weakened at all (cf. Fig. 7).

The extremely small rates for the oxidation or reduction reactions at low temperatures, are caused by the intricate

[1] Incidentally it may be emphasized that comparable phenomena have been observed by SNOEK in the field of magnetic forrites (J. L. SNOEK, New Developments in Ferro-magnetic Materials (1947) p. 97).

processes involved. The oxidation of manganese embedded in a lattice probably takes place according to the mechanism proposed by WAGNER for the oxidation of Cu_2O [1]. In the first stage of the process an oxygen molecule collides with the crystal and is loosely bound at the surface by VAN DER WAALS' forces. Now manganese ions inside the crystal, transforming into Mn^{3+} ions, provide electrons which travel to the surface and combine with the oxygen atoms to form oxygen ions. Due to this process, which may occur at every temperature, the surface is charged negatively with regard to the inside of the crystal, and this charge will stop further oxidation. Except by a return to the original state, the charge can only be neutralized — and so further oxidation made possible — by the diffusion of positive metallic ions (in our case Mg^{2+}, Ti^{4+} and to a negligible extent Mn^{2+} or Mn^{3+}) out of the inside of the crystal to the hole at the surface formed by the newly attached oxygen ion, finally leaving one of the metal positions unoccupied in the neighbourhood of the oxidized manganese ions. We might also describe the last stage of the process by stating that the unoccupied ionic position travels from the surface to an oxidized manganese ion, giving rise to the increased ratio between manganese and oxygen demanded by the oxidation.

It is the diffusion of the positive ions through the lattice which, being strongly temperature dependent, causes the freezing of the reaction at low temperatures.

When the temperature below which the oxidation is frozen in lies higher than the temperature at which the thermodynamic equilibrium permits the existence of ions of the higher valency state, no oxidized ions can occur. This — besides energetical reasons discussed in the previous paragraph (p. 63) — might very well be the reason that the manganese in most luminophors exists exclusively in the divalent state [2].

2.3 Chemical proof of the oxidation of manganese

Although the occurrence of an oxidation of our luminophors and even the existence of manganese of a higher valency has

[1] C. WAGNER, *Trans. Far. Soc.*, **34** (1938) 851.

[2] This view is supported by recent observations by FROELICH with Zn_2SiO_4–Mn. The manganese within the crystals is in the divalent state under all circumstances; the manganese near the surface, however, may be oxidized to a higher valency state by heating in an oxidizing atmosphere at a comparatively low temperature (H. C. FROELICH, *Trans. Elektrochem. Soc.*, **87** (1945) 429).

already been made probable by the experiments described in the previous section, we still have to deliver a conclusive proof. To this end we have made use of a chemical method which enabled us to determine the degree of oxidation of the crystals by means of their oxidizing power towards hydrogen chloride and potassium iodide.

In principle the method is extremely simple: the substance under consideration is dissolved in strong hydrogen chloride, so that oxidative oxygen liberates an equivalent amount of chlorine. By means of a stream of oxygen-free nitrogen the liberated chlorine is distilled into an acid solution of potassium iodide, where it in turn liberates iodine which may be titrated with sodiumthiosulphate.

Owing to the small quantities of oxidative oxygen to be detected, the experiment must be carried out with great care. Fig. 8 shows the most important section of the appa-
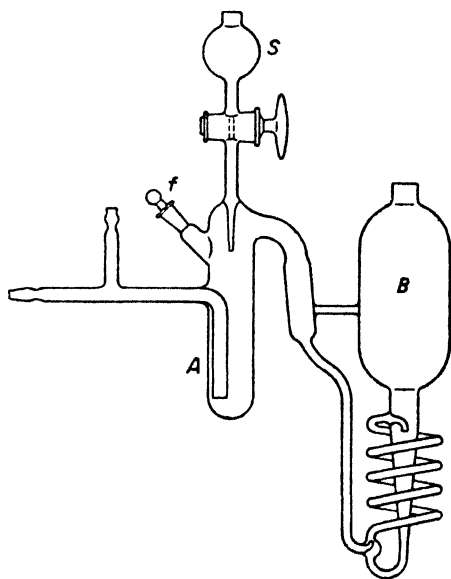
Fig. 8. Titration apparatus according to P. W. HAAYMAN and A. BOL.

ratus, which was designed by Dr P. W. HAAYMAN and Mr A. BOL of this laboratory. It consists of two parts. In *A* the

substance is dissolved, in *B* the titration takes place.

Detailed description of a determination:

1. Part *B* of the apparatus is filled with a solution of 2 g potassium iodide in 8 ml water.
2. About 0.25—0.5 grams of the powder to be investigated is introduced into *A* through the filling tube *f* by means of a specially designed funnel-shaped filling vessel. Weighing of this vessel, full before the transfer and nearly empty afterwards, gives the exact weight of the powder actually entering.
3. The separating funnel *s* of *A* is filled with 6 N hydrochloric acid.
4. By means of a rapid stream of pure nitrogen, completely freed from oxygen by passage through an alkaline solution of pyrogallol (120 g KOH and 5 g pyrogallol in 95 ml water) the air is driven out of the apparatus in about 0.5—1 hour. After the addition of 8 ml 2 N sulphuric acid and a few drops of a fresh solution of starch to the liquid in *B*, this liquid is probably coloured slightly violet greyish, or otherwise must be coloured in this way by the addition of one or two drops of a dilute iodine solution. The liquid is discoloured by a careful titration with a 0.001 N solution of sodium thiosulphate. This forms the zero of our determinations.
5. After the stream of nitrogen passing through the apparatus is slowed down to a rate of about 30 ml/min, about 4 ml of the 8 N HCl is run out of the separating funnel *f* onto the powder in *A*; then the temperature in this vessel is slowly increased to the boiling point. In this way the originally slightly pink coloured Mg_2TiO_4–Mn is decomposed, leaving behind a white precipitate, probably consisting of TiO_2 or basic titanium chloride. Simultaneously the reaction gases entering the liquid in *B* cause the occurrence here of a dark violet colouring. Provisionally the liquid is almost discoloured by a rapid titration with 0.001 N sodium thiosulphate solution. After about 15 minutes when no further change occurs, and consequently the dissolution must be finished, the small quantity of liquid in *A*, together with the white precipitate, is transferred to *B* by canting the apparatus and by successive washings with the liquid out of *B*. (This was found to be necessary because considerable quantities of the liberated chlorine remain absorbed to the precipitate). Then the stream of gas is accelerated and the mixed solutions are finally discoloured by a careful titration, carried out extremely slowly in order to ensure homogeneity in the titration vessel. The amount of sodium thiosulphate used during stage 5 of the determination gives the oxidation power of the dissolved powder.

We have carried through determinations with products of various manganese contents, prepared under the different conditions of atmosphere and temperature described previously.

In order to increase the precision, we have included in our measurements products containing up to fifty times as much manganese as is necessary to obtain the maximum of luminescence.

TABLE VI

OXIDATIVE POWER OF Mg_2TiO_4–Mn

At. Mn/mol Mg_2TiO_4	$1300°/N_2$ m. aeq. I_2 per mol Mg_2TiO_4	$1300°/O_2$, quenched m. aeq. I_2 per		$1300°/O_2$–48 h $560°/O_2$ m. aeq. I_2 per	
		mol Mg_2TiO_4	atom Mn	mol Mg_2TiO_4	atom Mn
0	0	0	0	0	0
2×10^{-4}	0	?	?	0.34 0.416	1.7 2.08
1.4×10^{-3}	0	1.15	0.82	1.5	1.07
2×10^{-3}	0	1.2	0.6	2.25	1.13
4×10^{-3}	0	2.72	0.68	4.64	1.16
6×10^{-3}	0	4.36	0.73	6.15	1.03
1×10^{-2}	0	10	1.—	15.9	1.59
2×10^{-2}	0	21.7 23.3	1.09 1.17	27.7 31.8	1.39 1.59
4×10^{-2}	0	40.7	1.02	53.9	1.35
8×10^{-2}	0	67.6	0.85	107	1.34

The results are assembled in Table VI. Products prepared in nitrogen show no oxidizing power at all. The products made under oxidizing conditions show oxidizing power in a nearly linear relationship with the manganese content, proving that it is actually the manganese which is oxidized. The oxidation is strong for the strongly luminescent products, optimally annealed at 560° C, and weaker for the faintly luminescent, quenched, products. For the quenched products, an oxidizing power is found varying from 0.6—1.17 per manganese atom, corresponding to manganese ions of a valency

between 2.6 and 3.2; for the optimally annealed products we find values between 1 and 2, leading to an ion of a valency between 3 and 4. Owing to the difficulties of diffusion in the oxidation reactions occurring at the comparatively low annealing temperature of 560° it might well be possible that with the annealed products the crystals are not homogeneously oxidized: the equilibrium may have been reached in a region near the surface of the crystals, but the inside may still be incompletely oxidized [1]. Therefore the valency found for the annealed products must be expected to be too low and probably must be replaced by 4, the products containing exclusively Mn^{4+} ions. To the quenched products this argument of course does not apply. The value of 2.6—3.2 found here must be explained by the assumption of a mixture of ions of different valencies, either Mn^{2+} and Mn^{3+} together with a small quantity of Mn^{4+}, or $Mn^{2+}+Mn^{4+}$. In any case Mn^{4+} must be present (cf. Section 2.4.1).

2.4 Optical properties

2.4.1 *The spectral distribution of the red emission*

The spectral distribution of the red emission of the oxidized products upon excitation by λ 3650 Å was measured photographically, with the aid of a reflection grating [2] (cf. Appendix, Section 1).

In Fig. 9*a* and 9*b* we give the emission spectrum of an optimally luminescent product (point *a*, Fig. 7) at room temperature and at —180° respectively, measured with the same slit width. Fig. 9*c* shows the low-temperature spectrum as measured with a finer slit, revealing much more fine structure. The spectrum consists of a strong doublet at 6526 and

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[1] An argument in favour of this supposition is provided by the observed decrease of the luminescence upon grinding. Whereas in the original state the inner parts of the crystals hardly contribute to the luminescence, since the exciting light does not penetrate deeply, after grinding the crystals are broken up and some of the exposed inner regions begin to play a part in the luminescence process, spoiling the originally strong luminescence.

[2] I am indebted for the measurements to Dr A. KRUITHOF Jr of this laboratory.
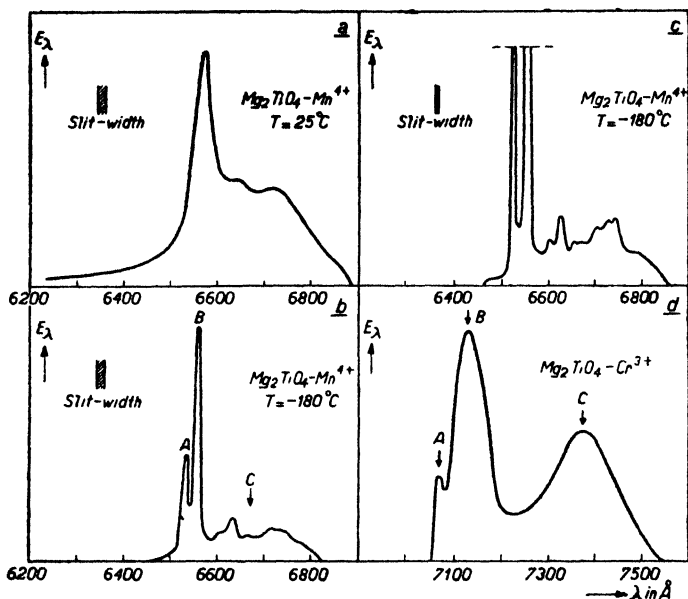
Fig. 9. Spectral distribution of the red luminescence of optimally annealed Mg_2TiO_4 – 0.002 Mn measured with different slit widths at 25° C or —180° C (*a*, *b*, *c*). In *d* we reproduce the emission band of Mg_2TiO_4–Cr according to O. Deutschbein, *Phys. Z.*, **33** (1932) 874.

6552 Å and some more weaker, overlapping bands at longer wave-lengths.

The spectrum of a faintly luminescent quenched product (corresponding to point *d* in Fig. 7) is shown in Fig. 10*a*,*b*; it is similar to that of Fig. 9, but is far more diffuse. Obviously it must be attributed to ions of the same valency (Mn^{4+}), but the circumstances under which each of these ions exist must be slightly different. In the strongly luminescent products (*a*, Fig. 7) all ions responsible for the emission must exist under exactly the same conditions: identical surroundings and hence identical electric fields thus giving rise to a comparatively sharp emission spectrum. In the quenched products however, the active activator ions must be under less defined conditions each emitting a slightly different emission and therefore
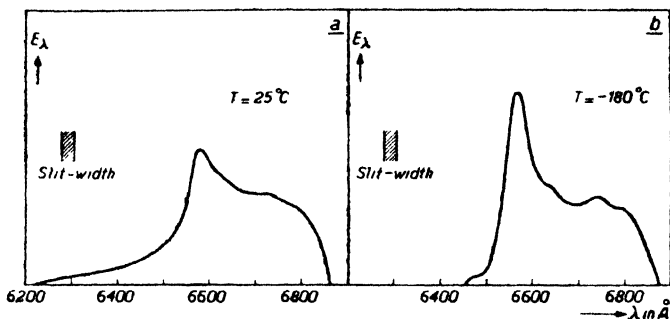
Fig. 10. Spectral distribution of the red luminescence of Mg_2TiO_4 — $0.002\,Mn$, quenched from 1200° C to room temperature, at 25° C (*a*) and —180° C (*b*).

together giving rise to a somewhat blurred emission. It seems reasonable to assume that in the first case the Mn^{4+} ions are placed at lattice positions in a normal, undisturbed lattice, in the latter case however near lattice flaws or in the surface of the crystals. As a matter of fact, it is probably only because of these exceptional positions that the existence of Mn^{4+} ions at the high temperature from which the quenching took place, is possible. Normally placed Mn^{4+} ions, for which according to Fig. 7 the equilibrium is shifted in the direction of lower valencies near 600° C, are only to be expected in negligibly small concentrations above 700° C, the main part of the manganese either being present as Mn^{2+} or as Mn^{3+}.

The attribution of the red luminescence to tetravalent manganese ions is further confirmed by a comparison of the emission spectrum with that of chromium. The electronic configurations of Mn^{4+} and Cr^{3+} being identical ($3\,d^3$), a great resemblance ought to exist between the spectra of these two ions, when placed in the same surroundings.

Fig. 9*d* shows the emission spectrum of Mg_2TiO_4–Cr^{3+} at a low temperature, according to DEUTSCHBEIN [1].

In Table VII we give for the spectra of Mg_2TiO_4–Cr^{3+} and Mg_2TiO_4–Mn^{4+} the wave-lengths and the wave numbers of some corresponding bands, namely the doublet (A, B) and the

[1] O. DEUTSCHBEIN, *Phys. Z.*, **33** (1932) 874.

TABLE VII

CORRESPONDING WAVE-LENGTHS AND WAVE NUMBERS IN THE SPECTRA OF Mg_2TiO_4 ACTIVATED BY TETRAVALENT MANGANESE OR TRIVALENT CHROMIUM

	Cr^{3+}		Mn^{4+}	
	Å	cm^{-1}	Å	cm^{-1}
A	7068	14 150	6526	15 323
B	7130	14 025	6552	15 262
C	7375	13 560	6675	15 000
A—B		125		61
B—C		465		262

centre of the long wave length part of the emission (C), and also the energy separations. The form of the spectra bears much resemblance. As far as the position on the wave-length scale is concerned, exactly as must be expected — and as was already found in the corresponding case of Sm^{2+} and Eu^{3+} [1] — owing to the higher charge of the core for Mn^{4+} the whole complex of bands of Mn^{4+} is situated at somewhat shorter wave lengths than that of Cr^{3+}.

2.4.2 *Reflection spectra*

The reflection of pure Mg_2TiO_4 and of oxidized and reduced products containing various amounts of manganese is shown in Fig. 11*a* and *b*. Unactivated Mg_2TiO_4 shows an absorption region with a long wave-length limit near 2800 Å. Upon introduction of manganese into the lattice an extra absorption occurs at the long wavelength side of the edge. For the oxidized, quenched products and the oxidized annealed products, the extra absorption is nearly the same; with the reduced products, containing Mn^{2+}, it is of the same kind but somewhat fainter, extending somewhat less into the visible. This may also be seen from the colour of the powders: Mg_2TiO_4 is white, the powders containing divalent manganese are coloured slightly greenish, while the oxidized products are either slightly red brown (quenched products) or red brown with a tendency towards pink (annealed products, tetravalent manganese).

[1] F. D. S. BUTEMENT–H. TERREY, *J. Chem. Soc. London* (1937) 1112.
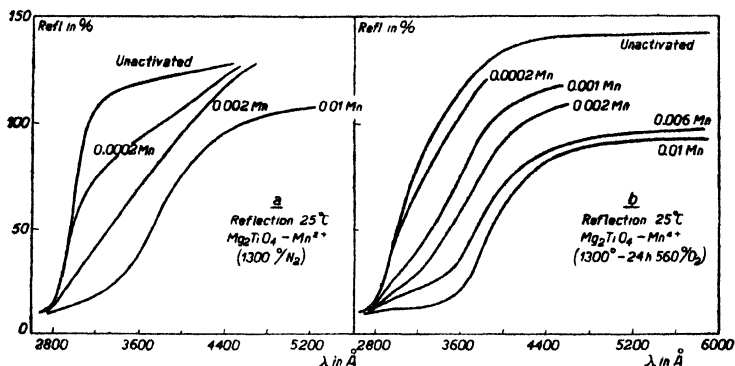
Fig. 11. Reflection spectra of $Mg_2TiO_4 - Mn^{2+}$ (*a*) and $Mg_2TiO_4 - Mn^{4+}$ (*b*) at 25° C. The manganese content is given in moles per mol Mg_2TiO_4.

The absorption bands correlated with the various manganese ions probably also extend to wave-lengths shorter than 2800 Å. Since they are covered in this region by the much stronger absorption of the matrix lattice, they cannot be observed.

2.4.3 *Excitation*

The red emission of the oxidized products is excited by radiations of a wave-length between 2600 Å and 6000 Å, obviously absorbed in the part of the extra absorption band correlated with Mn^{4+} which is not covered by the absorption of Mg_2TiO_4. The quantum efficiency of the process as a function of the wave-length is shown in Fig. 12: Maximum luminescence occurs upon excitation by λ 3250 Å, giving a quantum efficiency of 55%.

With both activated and pure Mg_2TiO_4, irradiation with $\lambda < 2800$ Å into the absorption region of the Mg_2TiO_4 causes no emission at room remperature, but gives rise to a green or blue luminescence at low temperatures (cf. Chapter V, concerning the luminescence of titanium).

With the reduced activated products at —180° C an extremely faint green luminescence is found upon irradiation into the absorption band of the divalent manganese (λ 2800—
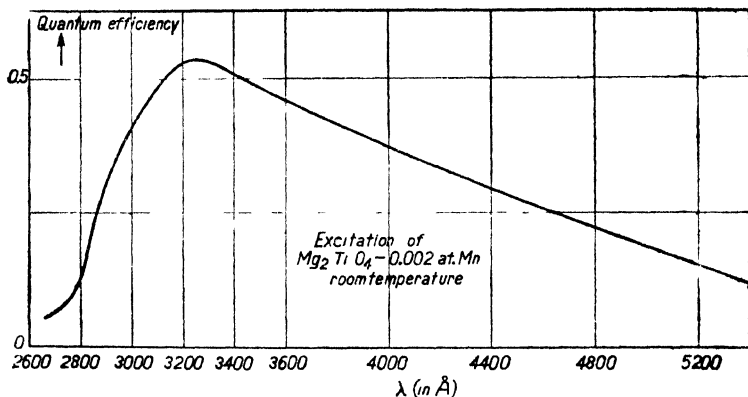
Fig. 12. Efficiency of the red luminescence of optimally annealed Mg_2TiO_4 - 0.002 Mn as a function of the wave-length of the exciting radiation (excitation spectrum).

4000 Å) which possibly indicates the occurrence of a green luminescence of normal intensity at still lower temperatures.

Indications for an emission due to Mn^{3+}, possibly present in the quenched oxidized products, were not found.

The red luminescence of the oxidized products is only faintly excited by cathode rays. The energy is mainly absorbed in the matrix lattice and is not transferred to the manganese.

2.4.4 *Dependence of the intensity of luminescence on the temperature*

For four different oxidized annealed products, corresponding to the points *a*, *b*, *c* and *d* in Fig. 7, the efficiency of the red luminescence upon irradiation with λ 3650 was measured as a function of the temperature. Fig. 13*a* gives the intensities in arbitrary units, the ordinates of the upper curve being put equal to 100. In order to show more clearly the differences between the shapes of the curves, in Fig. 13*b* the maxima of all curves are brought to the 100-level.

The sharp emission of sample *a*, due, according to Section 2.4.1, to Mn^{4+} ions at well defined positions, is nearly constant from low temperatures up to $\sim +60°$ C, diminishes slowly between 60° and 100° and falls suddenly above 100° to be
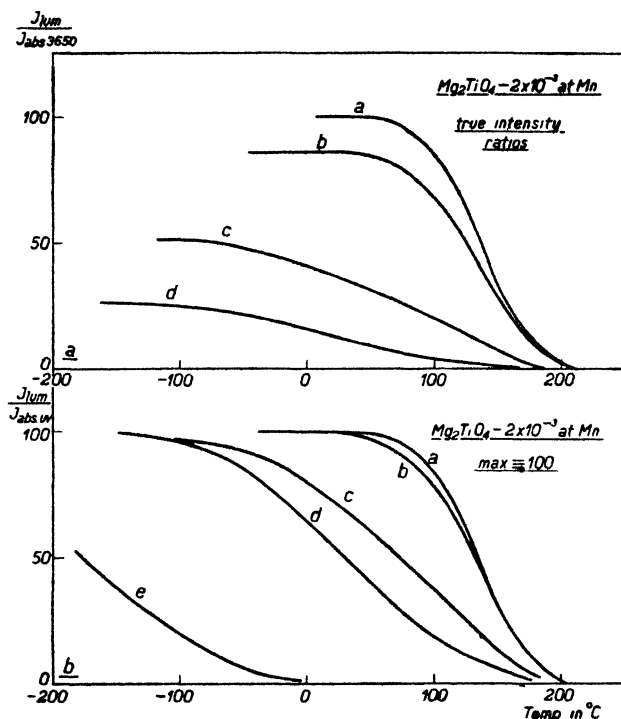
Fig. 13. Temperature dependence of the efficiency of the red luminescence of $Mg_2TiO_4 - 2 \cdot 10^{-3}$ Mn annealed for 48 hours at different temperatures, corresponding to the points *a*, *b*, *c* and *d* of Fig. 7; excitation by λ 3650 Å. Curve *e* gives the temperature dependence of the blue luminescence of Mg_2TiO_4, excited by λ 2537 Å.

13*a*. true intensity ratios (arbitrary units).
13*b*. maxima put equal to 100.

practically completely quenched at 200° C. For the diffuse emission of *d*, due to Mn^{4+} ions at badly defined positions, the decrease of efficiency sets in at a much lower temperature (—100°) and continues slowly over the whole temperature range. The samples *b* and *c* give curves of intermediate shapes.

For the oxidized annealed products the shape of the temperature-intensity curves is independent of the manganese con-

centration and is also unaffected by contamination with iron up to ten times the manganese content. Also variation of the intensity of the exciting radiation does not cause any change.

In Fig. 13*b*, curve *e* gives the temperature dependence of the blue emission of Mg_2TiO_4, excited by λ 2537 Å, showing the increase of intensity towards lower temperatures.

2.4.5 *The influence of the manganese concentration*

Fig. 14 shows the efficiency of the red luminescence of optimally annealed products excited with λ 3650 Å as a
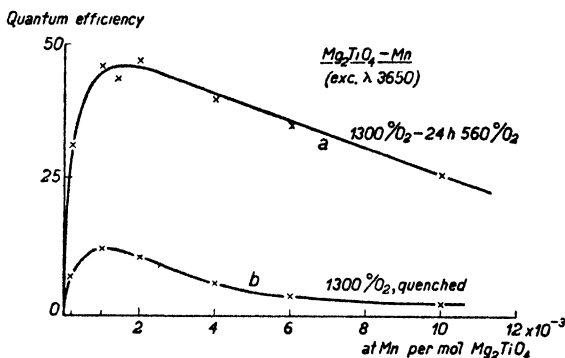
Fig. 14. Relative efficiency of the red luminescence of Mg_2TiO_4 — Mn at —180° C as a function of the manganese concentration.
a. optimally annealed (1300°/O_2 — 24 h. 560°/O_2).
b. quenched from 1300°/O_2 to room temperature.

function of the concentration of manganese. Maximum effects, corresponding to a quantum efficiency of 45% are found between a concentration of $1 \cdot 10^{-3}$ and $4 \cdot 10^{-3}$ at manganese per mol Mg_2TiO_4. On either side of this range the intensity falls, steeply on the side of lower concentrations, and much more gradually towards higher concentrations. The intensity for quenched products, measured at —180°, is also given. The emission of these products relative to that of the totally oxidized powders is strongest at low manganese concentrations and diminishes for the higher manganese contents. Since the emission of the quenched products was shown to be due to

Mn^{4+} at badly defined positions (cf. Section 2.4.1) present together with Mn^{2+} or Mn^{3+} at normal positions, this might be explained by the reasonable assumption that only a small fixed number of positions of this kind are available which may be occupied by the manganese. Thus the first manganese atoms incorporated in the crystal fill up these disturbed positions and may be oxidized to the tetravalent state. As soon as all these positions are occupied however — which probably occurs at a comparatively low manganese concentration — upon further increasing the manganese content, the newly introduced manganese ions have to occupy normal positions in the divalent or trivalent state. Here they cause an ineffective absorption coinciding with the excitation region of the Mn^{4+} and (cf. Sections 2.4.2 and 2.4.3) thus diminish the red emission of these ions.

2.4.6 *The intensity of the red emission of partly oxidized products*

From the foregoing it will be clear that the intensity of the luminescence of partly oxidized products (e.g., Fig. 7, *b*, *c*) wil be smaller than that of the totally oxidized systems for three reasons:

1. Mn^{2+} or Mn^{3+}, present together with Mn^{4+} cause a competing ineffective absorption in the excitation region of the Mn^{4+}.
2. the concentration of Mn^{4+}-ions is smaller.
3. the temperature quenching of the luminescence sets in at a lower temperature, due to the fact that of the fraction of manganese existing as Mn^{4+}, a relatively large amount is present at disturbed positions.

2.4.7 *The influence of iron*

The efficiency of the red luminescence is diminished by the presence of iron. Just as in the above case of the quenching effect of Mn^{2+} or Mn^{3+}, this effect is due to a competing ineffective absorption in the excitation region. As this iron-absorption happens to be rather faint in the region concerned, the decrease of efficiency is comparatively small: with samples containing 0.002 at Mn per mol Mg_2TiO_4, 0.002 and 0.01 at

Fe causes the efficiency to drop respectively to 90% and 50% of the value for the product containing no iron (excitation by λ 3650 Å). The temperature dependence is not affected.

2.4.8 *Decay of the red luminescence*

Dr DE GROOT and Dr SIMONS of this laboratory measured the decay of luminescence after interruption of the exciting radiation for the emission of Mn^{4+}. The process proves to be purely exponential with a time constant $\tau = 5 \cdot 10^{-4}$ sec.

3. THE LUMINESCENCE OF ALUMINIUM OXIDES ACTIVATED BY MANGANESE

3.1 Introduction

The data which are to be found in the literature concerning the luminescence of aluminium oxide activated by manganese are rather inconsistent. According to LECOQ DE BOISBAUDRAN [1], ARNOLD [2], SABURO IZAWA [3] and LENARD c.s. [4], the cathodo-luminescence is green. TIEDE and collaborators [5] report a predominantly red luminescence (extending from 5000 to 7000 Å with maxima at 6500 A[5a] or 6000 A[5b]). Both green and red bands next to each other were found by WIEDEMANN and SCHMIDT [6] and RANDALL [7], whereas IWASE [8] observed either green or red luminescence, depending on the manganese concentration.

We found in preliminary investigations that, besides the atmosphere of preparation (cf. Section 1), the chemical composition of the samples is also of great importance. In the

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[1] LECOQ DE BOISBAUDRAN, *C.R. Paris*, **103** (1886) 1107; **104** (1887) 330; **105** (1887) 261, 1228.
[2] W. ARNOLD, *Wied. Ann.*, **61** (1897) 318.
[3] SABURO IZAWA, *J. Soc. Chem. Ind. Japan*, **36** (1933) 43–44B
[4] LENARD–SCHMIDT–TOMASCHEK, *Handbuch der Exp. Physik*, 23/I, p. 425.
[5a] E. TIEDE–R. PIWONKA, *Ber. d. chem. Ges.*, **64** (1931) 2252.
[5b] E. TIEDE–H. LÜDERS, *Ber. d. chem. Ges.*, **66** (1933) 1681.
[6] E. EIEDEMANN–G. C. SCHMIDT, *Wied. Ann.*, **56** (1895) 201.
[7] J. T. RANDALL, *Proc. Roy. Soc. London* (A), **170** (1939) 291.
[8] E. IWASE, *Sc. Pap. Inst. Phys. Chem. Res. Japan*, **34** (1938) 761.

following we shall describe our results with pure aluminium oxide (α-Al_2O_3) and with aluminium oxide containing certain basic oxides (β-Al_2O_3 and γ-Al_2O_3).

3.2 α-Al_2O_3

3.2.1 *Preparation*

Crystalline aluminium oxide, the *X*-ray diffraction pattern of which revealed sharp lines of the pattern characteristic for the α-modification, was made by heating $Al(OH)_3$, precipitated from a solution of purified aluminium nitrate by means of ammonia, for one hour at a temperature between 1300 and 1500° C. The aluminium nitrate was p.a., RIEDEL DE HAEN pro analysis, freed from the last traces of heavy metals (transition elements, copper) by a treatment with cupferron. In order to obtain activated products containing a known amount of manganese, a dilute solution of manganese nitrate was added to a solution of the pure aluminium nitrate; after precipitation the mixture was dried on a water-bath and afterwards fired. The heating took place in a well defined atmosphere, either reducing (hydrogen or a mixture of hydrogen and nitrogen), or oxidizing (air or oxygen).

3.2.2 *Optical properties*

The white crystals of pure α-Al_2O_3 obtained in this way, are practically non luminescent under cathodic bombardment (4000 volts). The activated products, heated under reducing conditions are equally coloured white and do not show luminescence either at room temperature or at —180° C. When prepared in an oxidizing atmosphere, however, at room temperature as well as at —180° a faint red cathodoluminescence appears, extending from 6400—6650 Å with a maximum at about 6500 Å. Moreover the products have a colour, depending on the manganese content: slightly pink for the low concentrations ($\sim$ 1 mol ‰) to dark purple when more manganese is present (2 mol %).

In Fig. 15 we give the reflection spectrum for the various

products at room temperature. Unactivated α-Al_2O_3 and α-Al_2O_3–Mn fired under reducing conditions show the same reflectivity with no indication of absorption in the visible; at about 3000 Å a faint absorption sets in, probably the long wave-length extension of the fundamental absorption of
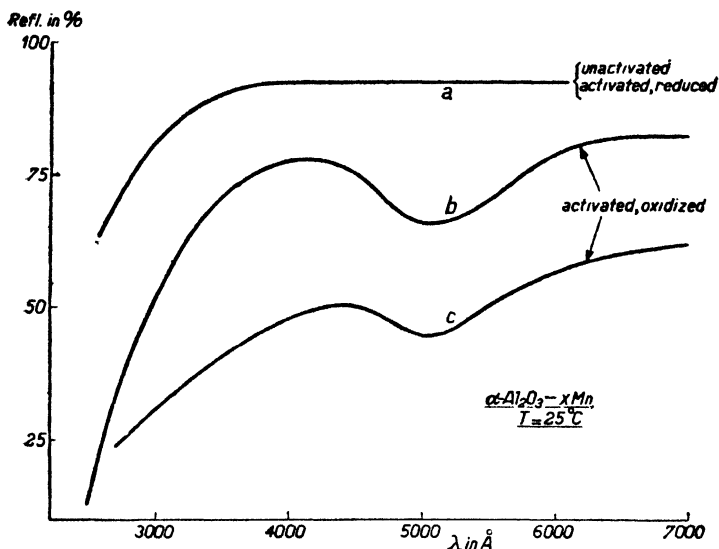
Fig. 15. Reflection spectra of αAl_2O_3–Mn at room temperature.
a. pure αAl_2O_3; αAl_2O_3 – 0.02 Mn^{2+}, 1500°/H_2.
b. αAl_2O_3 – 0.001 Mn, 1500°/O_2.
c. αAl_2O_3 – 0.01 Mn, 1500°/O_2.

α-Al_2O_3, the edge of which must be situated at 2800 Å [1] or 3000 Å [2]. For the activated products made under oxidizing circumstances the reflection clearly reveals an extra absorption band dependent on the manganese concentration: the absorption starts in the red at about 6000 Å, is maximum at about 5000 Å and decreases towards the blue. Yet, whereas a faint

[1] F. Möglich-R. Rompe, *Z. Phys.*, **119** (1942) 472.
[2] C. F. Goodeve-J. A. Kitchener, *Ttans. Far. Soc.*, **34** (1938) 903.

emission can be raised by electronic bombardment, irradiation into the new absorption band does not give rise to any luminescence. Thus, although both emission and absorption provide proof for the existence of manganese ions of a valency higher than two in the oxidized crystals, the ions concerned with each of these phenomena are probably not identical. In connection with the results obtained with Mg_2TiO_4 we suggest that the ions responsible for the emission are tetravalent ions, the ions causing the absorption band trivalent ions. Physicochemical arguments support this view: we must expect that in Al_2O_3, containing trivalent aluminium ions as constituents of the lattice, the trivalent manganese ions can be easily built in, while the tetravalent ions are under far worse conditions. Therefore, when the outward conditions allow it (oxidizing atmosphere) the greater fraction of a given manganese concentration will be oxidized to the trivalent state and only a small fraction — possibly only those situated near lattice flaws or other abnormal positions — to the tertavalent state. In accordance with this the extra absorption bands are very pronounced, the luminescence however is rather faint, at least much fainter than may be expected for a normal luminophor.

It is not impossible that Mn^{3+} and also Mn^{2+}, neither of which causes luminescence in the visible from 25° down to —180°, may give rise to luminescence at a still lower temperature. For Mn^{3+} the absence of emission may be only apparent, an emission possibly being situated in the infra red.

3.3 Other structures of aluminium oxide

3.3.1 *References*

As we have seen in the previous section, α-Al_2O_3–Mn does not show the green luminescence reported for aluminium oxide in the literature (cf. Section 3.1). A remark by LECOQ DE BOISBAUDRAN[1] stating the necessity of the presence of a small amount of potassium in the green luminescent aluminium oxides drew our attention to experiments regarding

[1] LECOQ DE BOISBAUDRAN, *C.R.Paris,* **105** (1887) 261.

TABLE VIII

Nr	Substance	Structure	Colour		Cathodo luminescence		Photo luminescence (λ 3650 Å)	
			ox. atm.	red. atm.	ox. atm.	red. atm.	ox. atm.	red. atm.
1	$CaO . 6Al_2O_3$–0.01 MnO	β	pink	white	red β^{I} + green	green	red β^{I}	—
2	SrO ,, ,,	β	,,	,,	,,	,,	,,	—
3	BaO ,, ,,	β	white	,,	green	,,	—	—
4	MgO ,, ,,	α+Spinel	rose	,,	red β^{II} + green	,,	red β^{II}	—
5	ZnO ,, ,,	α+Spinel	,,	,,	,,	,,	,,	—
6	$Na_2O . 11Al_2O_3$,,	$\alpha + \beta$	,,	,,	,,	,,	,,	—
7	K_2O ,, ,,	,,	,,	,,	,,	,,	,,	—
8	Li_2O ,, ,,	$\alpha + \gamma$	white	,,	green	,,	,,	—
9	$BeO . 6$,, ,,	α	,,	,,	red α	—	red α	—
10	PbO ,, ,,	,,	,,	,,	,,	—	,,	—
11	SnO ,, ,,	,,	,,	,,	,,	—	,,	—
12	CdO ,, ,,	,,	,,	,,	,,	—	,,	—
13	HgO ,, ,,	,,	,,	,,	,,	—	,,	—
14	$CaO . 5Al_2O_3 . P_2O_5$ 0.01 Mn	$\alpha + x$	pink	,,	red β^{II} + green	green	red β^{II}	—

the various crystal structures of aluminium oxide and their dependence on the composition, according to which small amounts of basic oxides cause the formation of different modifications of aluminium oxide: a new hexagonal structure, β-Al_2O_3 can be obtained with Na_2O and K_2O in amounts of 3.5 percent by weight [1] or by SrO, CaO, BaO and PbO in a quantity of one mol on six molecules of Al_2O_3 [2], and MgO also seems to stabilize this structure [3].

On the other hand with 0.35% lithium oxide a cubic structure is obtained [4], similar to those obtained by heating precipitated $Al(OH)_3$ at a temperature below 1000° C: γ-Al_2O_3 [5], or by anodic oxidation of aluminium: γ'-Al_2O_3 [6].

3.3.2 *Preparations*

It seemed worthwhile to make products containing different basic oxides in order to study their luminescent properties.

The method of preparation was similar to that employed for α-Al_2O_3: a mixture of solutions of the nitrates of aluminium, manganese and the elements concerned was precipitated by means of ammonia, dried on a water bath and heated succes-

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[1] W. L. Bragg–C. Gottfried–J. West, *Z. Kristallogr.*, **77** (1931) 255.
L. T. Brownmiller–R. H. Bogue, *Am. J. Sc.*, **23** (1932) 501; *Bur. St. J. Res.*, **8** (1932) 289.
C. A. Beevers–S. Brohult, *Z. Kristallogr.*, **95** (1936) 472.
C. A. Beevers–M. A. S. Ross, *Z. Kristallogr.*, **97** (1937) 59.

[2] K. Lagerqvist–S. Wallmark–A. Westgren, *Z. anorg. allgem. Chem.*, **234** (1937) 1.
V. Adelsköld, *Ark. Kem. Mineral. Geol.*, **12** (A) (1938) 9; *Strukt. Ber.*, VI (1938) 75.

[3] G. A. Rankin–H. E. Merwin, *J. Am. Chem. Soc.*, **38** (1916) 568.

[4] H. B. Barlett, *J. Am. Cer. Soc.*, **15** (1932) 361.
E. Kordes, *Z. Kristallogr.*, **91** (1935) 193.
E. J. W. Verwey, *Z. Kristallogr.*, **91** (1935) 65; *J. Chem. Phys.*, **3** (1935) 592.

[5] W. C. Hansen–L. T. Brownmiller, *Am. J. Sc.* (5), **15** (1928) 225.
F. Rinne, *N. Jahrb. Mineral.*, **58** (1928) 43.
W. Biltz–A. Lemke–K. Meisel, *Z. anorg. allgem. Chem.*, **186** (1930) 373.

[6] W. G. Burgers–A. Claassen–J. Zernike, *Z. Phys.*, **74** (1932) 593.

sively at 500° and 1500° C. The crystal structures of the products obtained were determined by the DEBYE–SCHERRER method of *X*-ray diffraction.

3.3.3 *Results*

In Table VIII the products prepared under both oxidizing and reducing conditions are listed, together with the crystal structure, their own colour and the colour of the luminescence. The systems containing PbO, SnO, CdO, HgO, BeO and MnO all show the pattern of α-Al_2O_3. CaO, SrO and BaO gave products consisting exclusively of crystals of the β-Al_2O_3 structure. Conglomerations of crystals of different crystal structures were observed with Na_2O and K_2O, Li_2O and ZnO and MgO. With potassium and sodium the coexisting phases were α-Al_2O_3 and β-Al_2O_3, with lithium α-Al_2O_3 + γ-Al_2O_3, whereas with zinc and magnesium the patterns of α-Al_2O_3 and spinel ($ZnAl_2O_4$ and $MgAl_2O_4$) were found next to one another.

While unactivated products are not influenced by different atmospheres of preparation, and in neither case show any colour or luminescence, in products containing manganese the optical properties again give clear indications of the occurrence of manganese of a valency higher than two. In contrast with the white reduced products, most of the products prepared under oxidizing conditions are coloured pink, due to an absorption band correlated with the oxidized manganese ions. In emission, besides the green bands, found especially with reduced products and hence connected with divalent manganese ions, red bands also occur which must be attributed to tetravalent or trivalent manganese ions.

The red emissions show three different spectral distributions: The first emission band, showing not much fine structure, is found with products 9—10—11—12 and 13 of Table VIII and — being obviously identical with the band described in the previous section — must be correlated with oxidized manganese, incorporated in α-Al_2O_3. The second band shows a fine structure, especially at —180° C (Fig. 16*a*). It is found with products containing Ca and Sr (1 and 2 of Table VIII)

and no doubt must be attributed to Mn^{3+} or Mn^{4+}, incorporated in β-Al_2O_3. Accordingly we call it red β^I. The third band,
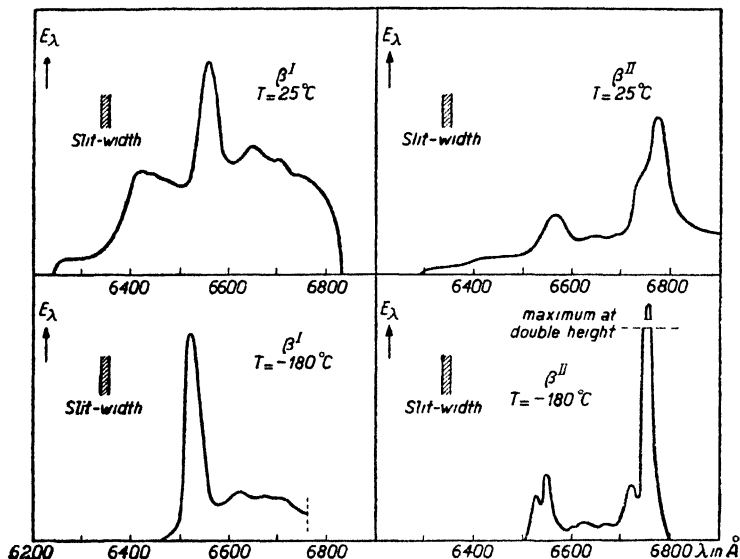
Fig. 16. Spectral distribution of the two different types of red luminescence of β–Al_2O_3 at room temperature and —180° C.
a. type β^I measured with $(0.9\ CaO - 0.1\ MgO) \cdot 6Al_2O_3 - 0.01$ at. Mn.
b. type β^{II} measured with $MgO.6Al_2O_3 - 0.005$ at. Mn.

equally showing a fine structure (Fig. 16*b*) was observed with products containing *Na, K, Mg, Zn* (4, 5, 6, 7 and 14 of Table VIII); it must be correlated with a crystal phase which, though the *X*-ray diffraction photographs do not reveal its presence in all cases [1], must be common to all products showing this emission. Obviously we have to make our choice between three possibilities, viz., β-Al_2O_3 as occurring with *Na* and *K*, spinel as occurring with *Mg* and *Zn* and an unknown structure *X*, the presence of which was indicated by some new lines on

[1] The emission being comparatively weak, it may very well be emitted by a fraction of the crystals, too small to be detected by means of its diffraction pattern.

the diffraction pattern of sample 14. Since the spinels show a red emission of still another type (cf. Section 4), and whereas the form of our emission shows much resemblance with the β^{I} emission, we are inclined to attribute it to β-Al_2O_3 too and refer to it as β^{II}. Differences between β^{I} and β^{II} are probably caused either by a slight difference in the β-structures concerned, or by a difference in the position of the manganese ions which are responsible for the emission.

In the following we shall give a detailed description of the chemical and optical properties of some of the preparations.

3.4 Ca–β-Al_2O_3

3.4.1 *Reduced products*

When prepared under reducing circumstances, $CaO.6Al_2O_3$–Mn
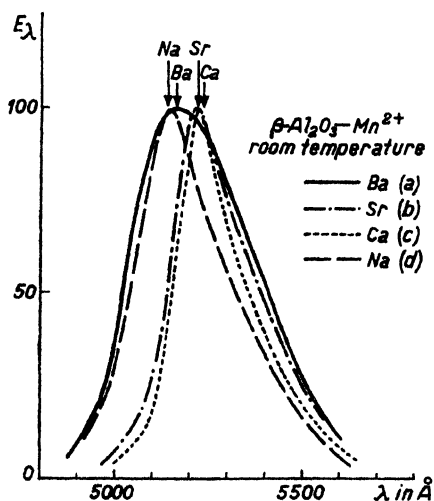
Fig. 17. Spectral distribution of the green cathodo-luminescence of β–Al_2O_3–Mn^{2+} at room temperature.
a. $BaO.6Al_2O_3$ – 0.005 Mn (1450°/N_2)
b. $SrO.6Al_2O_3$ – 0.005 Mn (1450°/N_2+H_2)
c. $CaO.6Al_2O_3$ – 0.01 Mn (1500°/N_2)
d. $Na_2O.11Al_2O_3$ – 0.01 Mn (1500°/N_2)

shows a green cathodo-luminescence in a broad band, extending from 5000 to 5700 Å with a maximum at 5230 Å, not showing any fine structure (Fig. 17).

The colour of the products remains nearly white even for the highest manganese content (2% *Mn*). The reflection
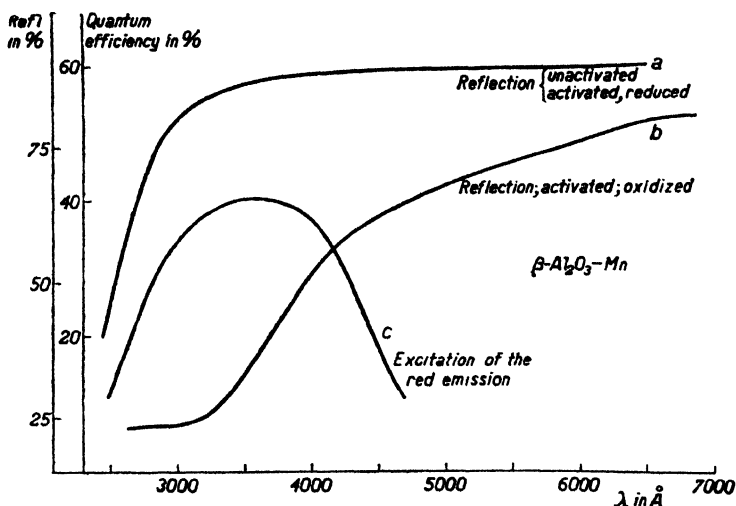
Fig. 18. Reflection and excitation spectra for $Ca–\beta Al_2O_3–Mn$ at room temperature:

a. reflection of $(0.9\ CaO–0.1\ MgO).6Al_2O_3$ and $(0.9\ CaO - 0.1\ MgO).6Al_2O_3 - 0.01\ Mn$, 1500°/$H_2$.
b. reflection of $(0.9\ CaO–0.1\ MgO).6Al_2O_3–0.01\ Mn$, 1500°/$O_2$.
c. excitation of the red luminescence of the product defined under *b*.

spectra, identical with that of the unactivated subsrance, reveal the existence of a strong absorption with a long wavelength limit at about 2400 Å (Fig. 18*a* [1]). In addition photographs of the absorption spectrum of thick powder layers (~ 1 mm) show a faint narrow absorption band at ~ 4260 Å, and photographs of the spectral distribution of the excitation indicate some more, equally narrow bands in the near ultra

[1] The reason for the presence of magnesium will be given furtheron.

violet. Obviously the broad absorption is the fundamental absorption of the matrix lattice, while the narrow bands are the characteristic absorption bands of divalent manganese (cf. Section 5 of this chapter).

Excitation of the green emission is possible by means of ultra-violet or blue light of the wave-lengths of the characteristic bands of Mn^{2+}, by electronic bombardment or by X-rays; no excitation occurs however on irradiation in the absorption region of the matrix lattice with radiation of a wave-length $\lambda < 2600$ Å.

3.4.2 *Oxidized products*

The products prepared under oxidizing conditions are coloured pink and show a red luminescence of the type β^I (Fig. 16) next to the green luminescence due to the divalent manganese. As may be concluded from reflection measurements (Fig. 18*b*) the colouring is caused by a broad extra absorption which begins in the visible at about 6600 Å and, increasing towards short wave-lengths, extends to the ultra violet. Though probably also existing in the region of wave-lengths shorter than 2600 Å, in this region it is negligible compared with the strong fundamental absorption of the matrix lattice and accordingly cannot be observed. The depth of the colour, or in other words, the strength of the absorption in the extra band is directly related to the manganese concentration. Although we did not determine the entire reflection curves for various manganese contents, measurements at one wave-length (λ 3650 Å), which certainly falls in the absorption band concerned, seem to be conclusive on this point (Fig. 19): the reflection is maximum for low concentrations of manganese and diminishes for increasing concentrations. Irradiation into the extra absorption band as far as it is not covered by the fundamental absorption of the matrix lattice, causes excitation of the red emission. Fig. 18 gives the quantum efficiency of this process as a function of the wave-length: excitation occurs between 6600 and 2600 Å with a maximum at about 3400 Å. Just as was observed with the reduced products, irradiation into the fundamental absorption does not give rise to lumines-

cence: the situation is comparable with that of Mg_2TiO_4–Mn, in which the energy absorbed in the absorption of the matrix lattice was also not transported to the activator.
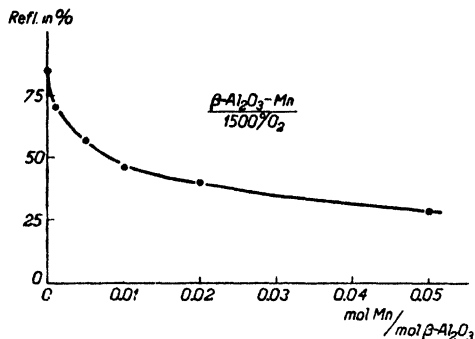
Fig. 19. Reflection of (0.9 CaO–0.1 MgO).6Al_2O_3–Mn (1500°/O_2) for λ 3650 Å, as a function of the manganese concentration.

Excitation by means of electronic bombardment gives rise to the emission of the red band and the green band simultaneously, proving the coexistence of manganese ions of different valencies. Apparently we are dealing here with the situation anticipated in our theoretical considerations of an equilibrium existing between the manganese in its various valency states (cf. Section 1).

The optical data mentioned above can be readily explained by the assumption that Mn^{2+} ions are responsible for the green emission and that one kind of oxidized ion is present to which both the red emission and the extra absorption must be attributed. Taking into account the resemblance between the red emission β^I and the red emission found with Mg_2TiO_4–Mn, we are inclined to believe that in this case also tetravalent manganese is responsible for the emission, and so we must assume a coexistence of $Mn^{2+} + Mn^{4+}$ ions.

As we saw already, the position of the equilibrium — i.e.,

the ratio between the quantities of divalent and tetravalent manganese co-existing — depends on the atmosphere of preparation, Mn^{4+} being only found in products made under oxidizing conditions. In addition the composition of the matrix crystal proved to be of very great importance. While
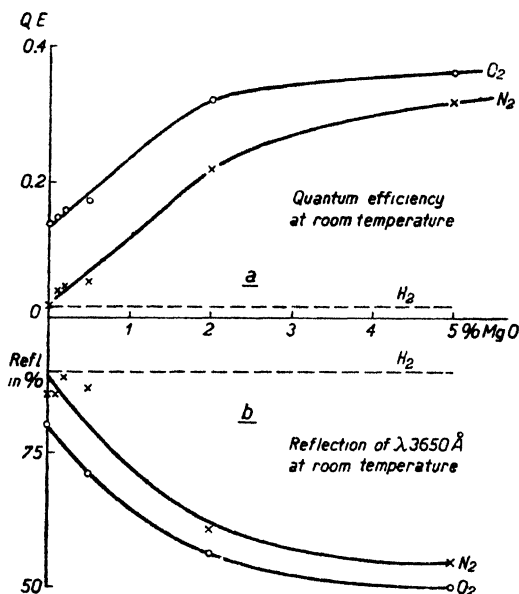
Fig. 20. Intensity of the red luminescence (*a*) and the reflection for λ 3650 A° (*b*) as a function of the magnesium content, for samples of $\{(1-x)\,CaO - x\,MgO\}.6Al_2O_3$-0.01 *Mn* prepared at 1500° C in an atmosphere of O_2, N_2 or H_2.

in $CaO.6Al_2O_3$-0.01 *Mn* even when prepared in pure oxygen the manganese seems to be oxidized only to a small extent, in products where part of the calcium is replaced by magnesium the manganese is oxidized much further: the latter crystals are coloured more deeply than the former and show the red emission in a much higher intensity [1].

[1] For this reason we used crystals of this composition in most of our measurements.

The influences of composition and atmosphere may be balanced against one another. In the presence of magnesium a much lower oxygen pressure is necessary for the occurrence of a certain degree of oxidation: $CaO.6Al_2O_3$-0.01 *Mn* is not luminescent when fired in nitrogen and shows only a faint emission when prepared in oxygen; the products containing magnesium however, already show a luminescence of this intensity when prepared in nitrogen.
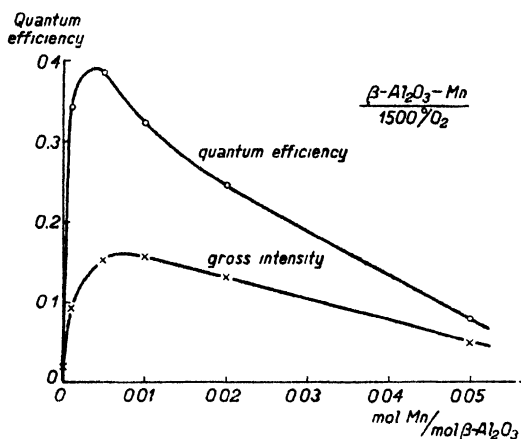
Fig. 21. Absolute efficiency and gross intensity of (0.9 *CaO*–0.1 *MgO*).$6Al_2O_3$–*x Mn* for excitation by λ 3650 A⁰ as a function of the manganese concentration.

Fig. 20 shows the influence of the magnesium concentration upon the intensity of luminescence for samples of one manganese content prepared in different atmospheres. In addition the reflection of λ 3650 Å for the same products is given, showing once more the close relationship between the absorption and the luminescence. Zinc causes effects similar to those of magnesium but to a somewhat smaller extent.

The quantum efficiency of the red luminescence excited by λ 3650 Å depends on the activator concentration in the normal way: in the region of low concentrations it increases continuously to reach a maximum and decreases again towards

higher concentrations. The optimum activator concentration for the quantum efficiency was found to be 0.003 mol manganese per mol β-Al_2O_3, differing slightly, owing to the varying absorption, from the value of 0.006 mol found for the optimum for the gross intensity (Fig. 21).

The temperature dependence of the red photo-luminescence
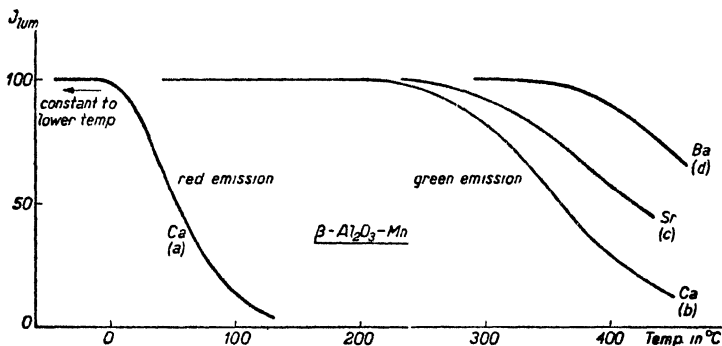
Fig. 22. Temperature dependence of the luminescence of β-Al_2O_3-Mn:

a. efficiency of the red emission of (0.9 CaO–0.1 MgO).6Al_2O_3 – 0.01 Mn (1600°/O_2) for excitation by λ 3650 Å.

b. intensity of the green cathodo-luminescence of (0.9 CaO–0.1 MgO).6Al_2O_3 – 0.01 Mn (1500°/N_2+H_2).

c. intensity of the green cathodo-luminescence of SrO.6Al_2O_3 – 0.005 Mn (1450°/N_2).

d. intensity of the green cathodo-luminescence of BaO.6Al_2O_3 – 0.005 Mn (1450°/N_2).

of an oxidized product of the composition (0.9 CaO-0.1 MgO) 6Al_2O_3-0.01 Mn and of the green cathodoluminescence of a reduced sample of the same composition is shown in Fig. 22.

The decay of the red luminescence (excited by λ 3650 Å) after interruption of the exciting radiation proved to be exponential with a time constant $\tau = 1.6 \cdot 10^{-3}$ sec [1].

[1] Measured by Dr W. de Groot of this laboratory.

3.5 $BaO.6Al_2O_3$ and $SrO.6Al_2O_3$

The properties of activated, reduced β-Al_2O_3 crystals containing *BaO* or *SrO* instead of *CaO* are much like those of $CaO.6Al_2O_3$–Mn^{2+}. Both are white, show a green luminescence of nearly the same spectral distribution (Fig. 17) and have similar excitation spectra.

The temperature dependence of the luminescence is slightly different in the three cases (Fig. 22). With *Ca*–β-Al_2O_3 the quenching of luminescence starts at 260° C, for *Sr* the temperature is somewhat higher (300° C) and for *Ba* still higher (380° C). Obviously the variation is a regular one, changing sympathetically with the other properties of the ions concerned such as ionic radius, atomic weight, atomic number, etc.

A similar variation of the properties of the matrix lattices finds a much more pronounced expression in the products made under oxidizing conditions. Here the degree of oxidation diminishes regularly from *Ca* towards *Ba*. The red luminescence and the corresponding absorption were found to be comparatively strong with $CaO.6Al_2O_3$–*Mn*, much fainter with $SrO.6Al_2O_3$–*Mn* and were not observed at all with $BaO.6Al_2O_3$–*Mn* (cf. Table VIII). Obviously the conditions for incorporating Mn^{4+} vary regularly in these three cases, offering another example of the influence of the nature of the matrix lattice on the position of the equilibrium in the oxidation reaction.

The stimulating effect of *MgO* and *ZnO* upon the oxidation of manganese found with $CaO.6Al_2O_3$, was also observed with $SrO.6Al_2O_3$ but not with $BaO.6Al_2O_3$; probably in the latter the conditions for Mn^{4+} cannot be improved to the extent necessary to make the existence of Mn^{4+} possible in this lattice.

For $SrO.6Al_2O_3$–*Mn*, oxidized with the aid of the presence of some magnesium oxide, the optical behaviour is exactly comparable with that for the corresponding calcium compound, spectra of excitation, absorption and emission being identical within the precision of the experiments[1].

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[1] The red fluorescence of other strontium aluminates activated by manganese, recently patented (H. C. FROELICH, *U.S.A. Pat. Spec.* 2.392.814) is also due to oxidized manganese.

3.6 γ-Al_2O_3

γ-Al_2O_3, made by heating a sample of $Al(OH)_3$, containing some manganese, at about 900° C, shows an orange luminescence when excited by λ 3650 Å or cathode rays. This is in contradiction to a statement by TIEDE and PIWONKA [1] according to which the γ-phase of Al_2O_3 should be free from luminescence. A product of the same structure, stabilized by lithium and made by heating of $Al(OH)_3$, LiF and some $Mn(NO_3)_2$ at about 1200° C, either in an oxidizing or in a reducing atmosphere is not excited by ultra violet radiation, but shows a strong green cathodoluminescence, independent of the atmosphere in which it was prepared. The spectral distribution of a sample is given in Fig. 24.

The luminescence proves once more to be far more susceptible to small changes than the X-ray diffraction pattern. The configuration of the oxygen is the same in the different products, much like that in spinel [2], and generates similar diffraction patterns.

The occurrence of luminescence due to Mn^{2+} seems to be coupled with the presence of monovalent and divalent positive ions in the lattice: α-Al_2O_3 does not show the green Mn^{2+}-fluorescence, but γ-Al_2O_3 stabilized by lithium and the true spinels containing magnesium or zinc do (cf. Fig. 24).

4. THE SPINELS

4.1 Preparation

$MgAl_2O_4$ and $ZnAl_2O_4$ pure and activated by manganese were made as previously described (Section 1).

4.2 The reduced state

The reflection spectra of the products containing divalent manganese are very much alike for $ZnAl_2O_4$ and $MgAl_2O_4$ and show much resemblance with those of β-Al_2O_3 (cf. Section 3.4). Together with a broad absorption region, with a long wave-length limit at ~ 2600 Å (also found with the unactivated samples, cf. Fig. 23), faint narrow bands occur, characteristic

[1] E. TIEDE–R. PIWONKA, *Ber. d. chem. Ges.*, **64** (1931) 2252.
[2] E. KORDES, *Z. Kristallogr.*, **91** (1935) 193.
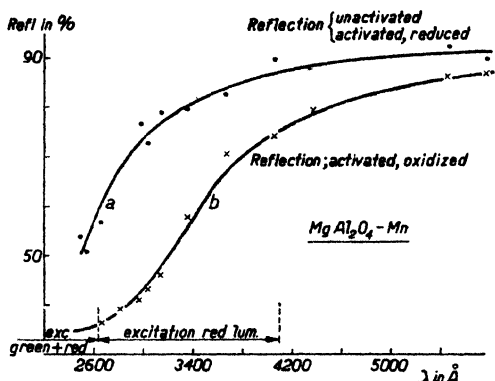
Fig. 23. Spectral distribution of the reflection and the excitation of luminescence of $MgAl_2O_4$–Mn:
a. reflection of unactivated $MgAl_2O_4$ and of reduced $MgAl_2O_4$–Mn $(1580°/N_2+H_2)$.
b. reflection of oxidized $MgAl_2O_4 - 0.002\,Mn$ $(1550°/O_2)$.
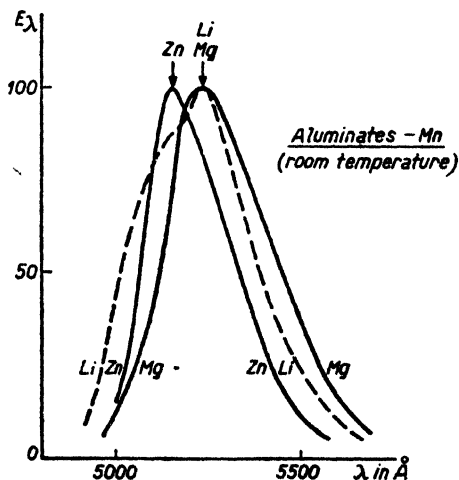
Fig. 24. Spectral distribution of the green cathodo-luminescence at room temperature of aluminates, activated by manganese:
$ZnAl_2O_4 - 0.01\,Mn$, $1470°/N_2$
$MgAl_2O_4 - 0.02\,Mn$, $1580°/N_2+H_2$
$Li_2O.11Al_2O_3 - 0.005\,Mn$, $1470°/N_2$ or O_2 $(= \gamma\,Al_2O_3)$.

of the ions of divalent manganese (cf. Section 5). For $ZnAl_2O_4$ these bands are situated at 2800, 3200, 3580, 3850 and 4340 Å, for $MgAl_2O_4$ at 2800, 3300, 3610 and 3800 Å.

Contrary to the case of β-Al_2O_3, excitation of a green luminescence occurs upon irradiation into both absorption regions: the manganese bands as well as the fundamental absorption of the matrix lattice. The same emission is also excited by cathodic bombardment or by X-rays. The spectral distribution of the bands at room temperature is given in Fig. 24: For $ZnAl_2O_4$–Mn the emission extends from 4900 Å to 5600 Å with a maximum at 5160 Å, for $MgAl_2O_4$–Mn from 4900 Å to 5750 Å with a maximum at 5230 Å.

4.3 The oxidized state

When prepared under oxidizing conditions, $MgAl_2O_4$–Mn and $ZnAl_2O_4$–Mn behave similarly as far as their reflection spectra are concerned. Both are slightly coloured ($MgAl_2O_4$ pink, $ZnAl_2O_4$ yellowish), due to the occurrence of an extra absorption band at the long wave-length side of the fundamental absorption, related to oxidized manganese. Fig. 23 shows the reflectivity for $MgAl_2O_4$–Mn.

The emission properties are quite different however. With $MgAl_2O_4$–Mn a red emission occurs which extends from 6400 to 7000 Å. At room temperature and better still at —180° C a fine structure can be observed. This emission is closely related to the extra absorption: Irradiation with $\lambda > 2600$ Å into that part of the extra absorption band not covered by the fundamental absorption gives rise to an emission in this band exclusively. Upon irradiation with ultra violet light of shorter wave-lengths, as well as with cathode rays or X-rays the red band of the oxidized manganese and the green band of divalent manganese are emitted simultaneously (cf. Fig. 23).

With oxidized $ZnAl_2O_4$–Mn however, even at —180° C no red emission can be observed [1]. The only emission occurring is the green one, due to Mn^{2+}. As the absorption spectrum

[1] The situation shows some resemblance to that of α-Al_2O_3 (Section 3.2) where the emission corresponding to the extra absorption band was also not observed.

proves the existence of oxidized manganese ions in the lattice, it remains possible that either an emission corresponding to that of $MgAl_2O_4$–Mn occurs at still lower temperatures or that an emission due to manganese in a different valency state occurs outside the visible (infra red). Considering the resemblance between the red emissions of $MgAl_2O_4$ and that of Mg_2TiO_4 and β-Al_2O_3 — all situated nearly identically on the wave-length scale — we are inclined to attribute the red emission and the corresponding absorption of oxidized $MgAl_2O_4$-Mn to tetravalent manganese here too. The optical properties are then explained by a coexistence of Mn^{2+} and Mn^{4+}. For $ZnAl_2O_4$ the existence of Mn^{3+} or Mn^{4+} together with Mn^{2+} both remain possible.

5. THE CHARACTERISTIC SPECTRA OF THE MANGANESE IONS ACTING AS AN ACTIVATOR

5.1 Divalent manganese

Luminophors containing divalent manganese all show comparatively narrow absorption bands in the visible and near ultra violet between 3000 and 4300 Å. As similar bands are observed with compounds of divalent manganese in the same spectral region at nearly identical positions [1] they must probably be ascribed to electronic transitions within the Mn^{2+} ions [2]. In Table IX we give a survey of these bands for some luminophors activated by manganese and some manganese compounds; the bands were observed either directly in absorption, or were found in the excitation spectra. According to TURNER and WEYL [3], divalent manganese in glass has an absorption band at 425 mμ.

Besides these relatively sharp bands, other, more diffuse bands occur rather more towards the red, which must equally

[1] J. GIELESSEN, *Ann. Phys.*, **22** (1935) 541.
[2] UEHARA ascribed these absorption bands to transitions in atomic manganese. It is hardly necessary to state that we are convinced that this is not correct.
(Y. UEHARA, *J. Chem. Soc. Japan*, **61** (1940) 741).
[3] W. E. S. TURNER–W. A. WEYL, *J. Soc. Glass Technol.*, **19** (1935) 208.

TABLE IX

CHARACTERISTIC BANDS OF DIVALENT MANGANESE

Wave-lengths in mμ

Absorption			Excitation					
$MnCl_2$–4aq	CdI_2–$MnCl_2$	$MnSiO_3$	$(Zn-Mn)_2SiO_4$	$(Zn-Be-Mn)_2SiO_4$	$(Zn-Mn)SO_4$	$(Zn-Mn)Al_2O_4$	$(Mg-Mn)Al_2O_4$	$(Cd-Mn)SiO_3$
				508				
				472.6				
			445	445				
	433	433		433		434		
	425–421.5	422.5	421	423	~420			
	416.4	407–417			~410			410
			385			385	380	
369		373.5	377	377	370			
363		361	361	361		358	361	350
342		343	341	335	347			
318		326. 319	320	320		320	330	
						280	280	

be attributed to the divalent manganese ions. Only with *ZnS–MnS* and *ZnS–CdS–MnS* do these bands show a more pronounced structure [1].

It is open to discussion whether these differences in sharpness justify attribution to electronic transitions of different types. If so, then the fact that the emission is found at the long wave-length side, immediately next to the last type of absorption bands indicates that the emission must be correlated with the diffuse bands.

The electronic configuration of the divalent manganese ion is characterized by a partly occupied $3d$–shell: $3d^5$. In principle two possibilities exist for excitation:

a. transitions within the $3d$-shell between different ground-states, i.e., between states with the same principal quantum number;

b. transitions from the d-shell to outer orbits.

The lowest ground-terms of d^5 for a free ion are ^6S, ^4G, ^4D, ^4P and ^4F. For incorporated ions these terms are split up due to the lattice field, except for the first one which remains unaffected. Hence excitation according to *a* could occur by transitions from the single ^6S state to one or more of the sub-levels of the other terms. Though the term-scheme is unknown even for the free ions, at least the situation of the corresponding terms for univalent chromium (*Cr* II, $3d^5$) and atomic manganese *Mn* I, $3d^5\ 4s^2$) [2] listed in Table X proves that the proposed transitions are of the right order of magnitude.

TABLE X

	^6S	^4G	^4P	^4D	^4F
Cr II ($3d^5$)	0	20 514	21 824	25 035	32 855
Mn I ($3d^54s^2$)	0	25 265	27 201	30 354	—

Data regarding transitions of the second type (*b*) are provided by MISS GILROY's[3] analysis of the spectrum of Mn^{2+}; some

[1] F. A. KRÖGER, *Physica*, **6** (1939) 369; **7** (1940) 92.
[2] M. A. CATALÀN–M. T. ANTUNES, *Z. Phys.*, **102** (1936) 432.
[3] H. T. GILROY, *Phys., Rev.*, **38** (1931) 2228.

approximate values, taken from her paper, are given in Table XI. At first sight even the cheapest transition here

TABLE XI

Transition in the Mn^{2+} ion	Wave-number cm^{-1}	Wave-length in Å
$3d^5 \rightarrow 3d^4 4s$	~ 58 000	1720
$3d^5 \rightarrow 3d^4 4p$	~ 108 000	920
$3d^4 4s \rightarrow 3d^4 4p$	~ 42 000–52 000	2 350–1 920
$3d^4 4p \rightarrow 3d^4 4d$	~ 58 000–62 000	1 700–1 600

($3d^5 \rightarrow 3d^4.4s$) seems to take too much energy. For the corresponding case of trivalent cerium, however, the transitions responsible for the absorption at 3000 Å = 33 000 cm^{-1} are supposed to occur between ^2F and one of the STARK levels of ^2D, while the separation of ^2F and ^2D in the free ion was found to be 50 000 cm^{-1}.[1,2]

Although the discrepancy is somewhat greater in our case, the attribution mentioned might yet be possible. We are therefore inclined to attribute the sharp absorption bands of Mn^{2+} to transitions $3d^5 \rightarrow 3d^5$ ($^6S \rightarrow$ STARK-levels of ^4G, ^4D, etc.) and the broader diffuse absorption bands, including the emission, to the transitions $3d^5 \rightarrow 3d^4.4s$. The comparatively large variations of emission caused by differences in the surroundings[3] of the manganese ions (e.g., $(Zn\text{–}Be)_2 SiO_4\text{–}Mn$) would then be explained at the same time, the outer orbits obviously being influenced to a much greater extent than the orbits of electrons in the *d*-shell.

BUTLER[4] ascribed the fluorescence of manganese in zinc silicate to the transition $3d^4 4p \rightarrow 3d^4 4s$. If this would be

[1] S. FREED, *Phys. Rev.*, **38** (1931) 2122.
D. M. BOSE–S. DATTA, *Nature* (London), **128** (1931) 270.
,, ,, *Z. Phys.*, **80** (1933) 376.
D. M. BOSE–P. C. MUKHERJE, *Phil. Mag.*, **26** (1938) 757.
[2] R. J. LANG, *Canad. J. Res.*, **13A** (1935) 1; **14A** (1936) 127.
,, *Phys. Rev.*, **49** (1936) 552.
[3] cf. S. H. LINWOOD–W. A. WEYL, *J. Opt. Soc. Am.*, **32** (1942) 443.
[4] K. H. BUTLER, *J. Opt. Soc. Am.*, **37** (1947) 566.

the case the fluorescence would not be excited by visible radiation, while excitation by long-wave ultra violet ($\lambda = 3650$ Å) would be a two-step process: $3d^5 \rightarrow 3d^44s \rightarrow 3d^44p$, which would cause of quadratic dependence on the exciting intensity. Neither of these two consequences agree with experiment; the fluorescence excited by λ 3650 Å varies linearly with the intensity of the ultra violet, while excitation by blue light has been observed [1]. That the excited absorption is only very weak is not surprising, for the transitions in the Mn^{2+} ions are forbidden, as is also indicated by the long decay times of the manganese fluorescence (~ 0.01 sec).

According to RANDALL [2] the influence of the surroundings is so great in some cases (e.g., Zn_2SiO_4–Mn) that it is not permissible to consider the luminescence effects as being characteristic of the Mn^{2+} ions. For these cases RANDALL assumes a sort of complex formed by the Mn^{2+} ion and the surrounding ions. As we saw previously for Tl^+ (Chapter I, Section 9) it may be extremely difficult to decide whether a complex or a perturbed ion must be accepted as a model; it is more or less a matter of taste. Considering the general character of the absorption and emission connected with manganese in luminophors, we prefer the single ion as a model in all cases, assuming an extra strong perturbation of the ion by its surroundings where this seems necessary.

5.2 Tetravalent manganese

For the attribution of the emission of tetravalent manganese to certain electronic transitions, we can make use of considerations made for trivalent chromium in a similar connection. Both Mn^{4+} and Cr^{3+} have the same electronic configuration $3d^3$ and behave optically in the same way (cf. Section 2.4.1). DEUTSCHBEIN [3], comparing the emission spectrum of Al_2O_3–Cr with the term-scheme of free Cr^{3+} ions,

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[1] F. A. KRÖGER, *Physica*, **6** (1939) 764; *Dissertation* Amsterdam (1940).

[2] J. T. RANDALL, *Proc. Roy. Soc. London (A)*, **170** (1939) 272.

[3] O. DEUTSCHBEIN, *Ann. Phys.*, **14** (1932) 729.
,, ,, ,, **20** (1934) 828.
,, *Z. Phys.*, **77** (1932) 489.

found the wave-length of two comparatively sharp lines of Al_2O_3–Cr to be nearly identical with the distances between the terms of ^2G and ^4F of the free ions and accordingly attributed the emission of the luminophor to transitions between these terms. This assumption is liable to a serious objection. Calculations by FINKELSTEIN and VAN VLECK [1] of the term-scheme of chromium in alumns showed that the various groundstates ^4F, ^2G, ^2H, etc., of the free ion are split up in the lattice field to such an extent that the splitting is greater than the mutual distances between the original terms. Sub-levels originating from different terms are mixed up and thus completely loose their identity.

Since with Al_2O_3–Cr and the spinels the fields are probably still stronger than in the alumns, certainly no terms are to be expected here corresponding to ^4F and ^2G. Furthermore the correspondence between the transition ^4F–^2G and the emission of luminophors seems to hold for Al_2O_3–Cr only, and not for other systems: for Mg_2TiO_4–Cr^{3+} for instance the discrepancy is considerable (emission $\sim$ 7100 Å, ^4F–^2G = 6700 Å). For Mg_2TiO_4–Mn^{4+} a correspondance of this kind is not even indicated (emission $\sim$ 6500 Å, ^4F–^2G = 5550 Å)[2]. Therefore the coincidence observed with Al_2O_3–Cr must have been purely accidental and accordingly DEUTSCHBEIN's attribution must be rejected. SPEDDING and NUTTING [3] came to the same conclusion on account of magnetic measurements.

In this connection, we are at the moment only able to make the general statement that the emission must be attributed to a transition involving levels originating from the terms of the free ions by a splitting of these terms in the extremely strong electric fields of the lattice.

[1] R. FINKELSTEIN–J. H. VAN VLECK, *J. Chem. Phys.*, **8** (1940) 790.

[2] H. E. WHITE, *Phys. Rev.*, **33** (1929) 676.
R. F. BACHER–S. GOUDSMIT, *Atomic Energy States*, New-York–London (1932), p. 166 and 285.

[3] F. H. SPEDDING, *Phys. Rev.*, **43** (1933) 143.
F. H. SPEDDING–G. C. NUTTING, *J. Chem. Phys.*, **2** (1934) 428.

III. TUNGSTATES AND MOLYBDATES

1. INTRODUCTION

As may be seen from Table III (Chapter I), tungstates and molybdates show luminescence. The emission occurring in each group is always found in about the same spectral region. Yet there are variations in the spectral distribution of the emission of the various members of a group: $CaWO_4$ and $SrWO_4$ for instance show luminescence in a blue band, $CdWO_4$, $MgWO_4$ and $ZnWO_4$ in a green band. Similar differences of colour occur with the molybdates. The intensities of the emissions vary within wide limits: $MgWO_4$ and $CaWO_4$ show an extremely strong luminescence (quantum efficiency for excitation by λ 2537 Å $\sim$ 70% [1]), $SrWO_4$ shows a much fainter emission, while $BaWO_4$ and Li_2WO_4 do not show any luminescence at all.

Precise data concerning the absorption of solid tungstates are not available; it is only known that absorption occurs in the near ultra violet. Solutions of alkali tungstates show an absorption edge at 2500—3000 A [2].

For the molybdates data are available for crystals as well as solutions. With ortho-molybdates in both cases absorption bands with a long wave-length limit near 3000 Å were observed [2c, 3, 5] and with di-molybdates an edge was found at about 3600 Å [3, 4, 5].

These last data make it extremely probable that the absorp-

[1] R. P. Johnson, *Am. J. Physics.*, **8** (1940) 143.
[2] *a.* S. Kato, *Sc. Pap. Inst. Tokio*, **13** (1930) 9.
b. H. Schulz–G. Jander, *Z. Anorg. Chem.*, **162** (1927) 141.
c. G. Jander–H. Witzmann, *Z. Anorg. Chem.*, **215** (1933) 318.
d. G. Jander–H. Mojert–Th. Aden, *Z. Anorg. Chem.*, **180** (1929) 146.
[3] Z. Soubarew–Chatelain, *C. R. Paris*, **206** (1938) 669; **207** (1938) 580.
[4] F. Hoermann, *Z. Anorg. Chem.*, **177** (1929) 156.
[5] M. Copeaux, *Ann. Chim. Phys.*, (8) **25** (1912) 39.

tion of the molybdates is of the characteristic type, caused by electronic transitions in the molybdate groups. Hence, presumably, the same applies to the tungstates. On the other hand, it is tempting to correlate the emissions with the same groups.

In the following we have studied the spectra of absorption and emission for a number of different tungstates and molybdates in order to ascertain whether a common relationship exists between these two phenomena, as would be expected if both originate from the same ion.

As was already stated above, for some of the tungstates and molybdates the emission is only faint or is not observed at all. These intensity differences proved to be due to temperature-quenching: in most cases lowering of the temperature to —180° caused a considerable increase of the intensity. In the few cases where no luminescence occurs even under these circumstances, an emission may be expected at still lower temperatures. Special attention has been paid to this point in Section 4 of this chapter.

2. PREPARATION

Compounds of the binary systems of WO_3 or MoO_3 with CaO, SrO, BaO, MgO, ZnO, CdO, PbO, Na_2O and Li_2O have been prepared from tungstic acid (H_2WO_4) or molybdic acid (H_2MoO_4) and compounds of the basic oxides mentioned which decompose easily (carbonates, acetates). These substances were mixed in the quantities necessary to give the desired compounds, moistened with water, dried on a water-bath and then heated for some hours at a temperature near — but always below — the melting point. The presence of free MoO_3 and WO_3 being inconvenient because of their troublesome absorption, we always used a small surplus of basic oxide above the stoechiometric composition.

In the preparation of $BaWO_4$, $SrWO_4$ and $CaWO_4$, according to an American invention[1] some sulphuric acid was added;

[1] W. A. ROBERTS, *U.S.A. Pat. Spec.* 2.312.267.

TABLE XII

Substance	Temp. of prep.	Crystal structure	Emission excited by λ 2537 Å at: room temp.	Emission excited by λ 2537 Å at: −180°	Abs edge (−180°) Å	Abs edge (−180°) cm⁻¹	Max. of emission (−180°) Å	Max. of emission (−180°) cm⁻¹	Difference abs.edge−max. of emission cm⁻¹
$BaWO_4$	1100	scheelite	—	—	2350	42 550	(3780)	26 455	16 095
Ba_2WO_5	1100	Ba_2WO_5	—	*m.* blue	3170	31 550	4350	22 990	8 560
$CaWO_4$	1100	scheelite	*s* blue	*s.* blue	2465	40 570	4200	23 810	16 760
Ca_3WO_6	1100	Ca_3WO_6	*f.f.* blue	*s.* blue	3010	33 220	4270	23 420	9 800
$CdWO_4$	1100	$CdWO_4$	*s.* blue-green	*s.* blue-green	3030	33 000	4930	20 280	12 720
Li_2WO_4	650	phenakite (= Be_2SiO_4)	—	*m.* blue	2800	35 720	4500	22 220	13 500
$Li_2W_2O_7$	650	$Li_2W_2O_7$	—	*m.* blue	2800	35 720	4500	22 220	13 500
$MgWO_4$	{1350	α-$MgWO_4$	—	*f* blue	2760	36 230	4180	23 930	12 300
	{1100	β-$MgWO_4$ = wolframite	*s.* blue-green	*s.* blue-green	2925	34 190	4940	20 240	13 950
Na_2WO_4	450	Na_2WO_4	—	—	2200	45 450	u.v.?	?	?
$Na_2W_2O_7$	650	$Na_2W_2O_7$	*f.f.* green	*s.* green	3000	33 330	5180	19 305	14 025
$PbWO_4$	1100	scheelite	*f.* green	*s.* blue	{3010	33 220	5220	19 160	14 060
					{(2900)	(34 480)	4350	22 990	11 490
$SrWO_4$	1100	scheelite	*f.* blue	*s.* blue	2425	41 240	4100	24 390	16 850
Sr_2WO_5	1100	Sr_2WO_5	—	*s.* green	3050	32 790	5000	20 000	12 790
Sr_3WO_6	1100	Sr_3WO_6	—	*s.* green	3115	32 100	5120	19 530	12 570
$ZnWO_4$	1100	wolframite	*s.* blue-green	*s.* blue-green	2980	33 560	4930	20 280	13 280

s = strong *m* = medium *f* = faint *f.f.* = very faint.

TABLE XIII

Substance	Temp. of prep.	Crystal structure	Emission excited by 2537 Å at:		Abs. edge (−180°)		Max. of emission (−180°)		Difference cm⁻¹ abs.edge−max. of emission
			25° C	−180° C	Å	cm⁻¹	Å	cm⁻¹	
$BaMoO_4$	700°	scheelite	—	—	2800	35 714	—	—	
Ba_3MoO_6	950°	$BaMoO_4$ + Ba_4MoO_7(?)	—	—	3850	26 000	—	—	
$CaMoO_4$	700°	scheelite	*f.* yellow	*s.* yellow	2925	34 190	5350	18 690	15 500
$CdMoO_4$	750°	scheelite	,,	,,	3330	30 000	5600	17 860	12 140
Li_2MoO_4	650°	phenakite	—	*f.f.f.* yellowish	2770	36 100	—	—	—
$Li_2Mo_2O_7$	530°	$Li_2Mo_2O_7$	—	*f.f.* orange	3400	29 410	6100	16 400	13 010
$MgMoO_4$	950°	$MgMoO_4$	—	—	2850	35 090	—	—	
$MgO.(MoO_3)_{1+x}$	950°	$MgMoO_4$	—	*f.* orange	$>$ 3650	$<$27 400	?	?	
$MgMo_2O_7$	600°	$MgMo_2O_7$(?)	—	*m.* or-yellow	3150	31 746	5950	16 780	14 966
$MgMo_3O_{10}$	600°	$MgMo_3O_{10}$ (?)	—	—	3500	28 570	—	—	
Na_2MoO_4	600°	Na_2WO_4	—	*f.f.f.* white	2660	37 600	—	—	—
$Na_2Mo_2O_7$	570°	$Na_2W_2O_7$	—	*m.* orange	3400	29 410	6300	15 850	13 560
$PbMoO_4$	850°	scheelite	—	*m.* yellow-green	3600	27 780	5120	19 530	8 250
$SrMoO_4$	700°	scheelite	—	*m.* yellow	2900	34 480	5300	18 870	15 610
Sr_3MoO_6	950°	Sr_3MoO_6	—	—	4100	24 400	—	—	
$ZnMoO_4$	950°	$ZnMoO_4$	—	—	2850	35 090	—	—	
$ZnO.(MoO_3)_{1+x}$	950°	$ZnMoO_4$	—	*m.* yellow	3200	31 250	5720	17 485	13 765

s = strong *m* = medium *f* = faint *f.f.* = very faint.

the surplus of basic oxide is then bound as sulphate, thus preventing the formation of compounds containing more basic oxide.

In Table XII and XIII we give the compounds prepared, identified by means of *X*-ray diffraction photographs.

In the systems of WO_3 and *CdO, ZnO, PbO* and *MgO* only one compound occurs, corresponding to the ortho composition (one mol WO_3 on one mol basic oxide). $MgWO_4$ exists in two modifications: an α-modification which is stable above 1250° C and a β-modification which is stable below this temperature [1]. By quenching from the high temperature, the α-form can be obtained at room temperature [2].

In the systems WO_3+CaO, *SrO* and *BaO*, beside the ortho-tungstates compounds occur containing a higher amount of basic oxide [3]; with Na_2O and Li_2O di-tungstates occur together with ortho-tungstates (Table XII). [4]

In the molybdate systems *CaO, SrO, BaO, PbO, CdO, ZnO. MgO*, Na_2O and Li_2O form ortho-molybdates. With *SrO* and

[1] The non-luminescent α-modification was first observed by miss HÜNIGER, citied by K. BIRUS, *Ergebn. Exakt. Naturw.*, **20** (1942) 221.

[2] C. G. A. HILL, *Trans. Far. Soc.*, **42** (1946) 685 has found a third modification by preparing $MgWO_4$ at 300° C. A fourth modification obtained at 600° C is probably identical with the α-form which — though being unstable at this temperature — may be formed for kinetical reasons. *X*-ray data for the various structures have been given by N. J. DUNNING–H. D. MEGAW, *Trans, Far. Soc.*, **42** (1946) 705.

Further it may be emphasized that a compound of the composition Mg_2WO_5 as reported in a paper by G. R. FONDA, *J. Phys. Chem.*, **48** (1944) 303 does not exist. The non-luminescent tungstate found is undoubtedly α-$MgWO_4$. cf. also R. NAGY–CHUNG KWAI LUI, *J. Opt. Soc. Am.*, **37** (1947) 37.

[3] Ca_3WO_6 has also been found by H. P. ROOKSBY and E. G. STEWARD, Nature **157** (1946) 548.

These authors mention also mixed crystals of this compound with the corresponding compounds of *Ba, Sr* and *Mg*.

Fluorescence properties of there products are mentioned by A. H. MCKEAG and P. W. RANBY, *Brit. Pat. Spec.*, 526.675; *U.S.A. Pat. Spec.* 2.257.699 and also by F. A. KRÖGER, *Philips Res. Rep.*, **2** (1947) 183.

[4] According to SILLEN and LUNDSBORG, *Arkiv. Kemi-Mineral.* **A 17** (1943), ref. *Chem. Abstr.*, **41** (1947) 1146, lead c orm the compounds Pb_2WO_5 and Pb_2MoO_5.

BaO compounds containing more basic oxide also exist, whereas Na_2O and Li_2O form di-molybdates and MgO probably a di- and a tri-molybdate. There are indications that $ZnMoO_4$ and $MgMoO_4$ are able to dissolve some MoO_3 in excess of the stoechiometric composition without changing their crystal structure (Table XIII).

3. ABSORPTION, EXCITATION AND EMISSION

For the substances described above we have determined the position of the absorption edges by means of reflection measurements. In the tungstates the edges varied from 2200 to 3100 Å, in the molybdates from 2750 to 4000 Å.

Provided the temperature is sufficiently low to make the occurrence of luminescence possible, emission is excited by irradiation into the entire absorption region. Usually all methods of excitation cause the emission of one and the same emission band. Only with $PbWO_4$ is the situation more complicated: At —180° C two different emissions occur, a blue one and a green one. The blue band is excited by radiation of a wave-length $\lambda < 2900$ Å, the green band especially by light of $\lambda > 2900$ Å, but to a smaller extent also by shorter wave-lengths. (Cf. Section 5). This is to be explained by the assumption of two partly overlapping absorption bands. The first band is strong, has a long-wave limit at 2900 Å and is correlated with the blue emission. The second absorption is somewhat fainter; it exists also in the region covered by the first band, but extends to longer wave-lengths (3050 Å). This band is correlated with the green emission. The reflection curve indeed shows some irregularities which may well be in accordance with this view.

The spectral distribution of the emission at —180° C was measured photographically; in nearly all cases the luminescence was excited by ultra violet radiation of λ 2537 Å. Only with $PbWO_4$ was the green emission excited by λ 3130 Å. Instead of $BaWO_4$, where even at —180° the emission is already quenched by interaction with the lattice, we measured the emission of a product containing 1 mol % $PbWO_4$. According to Section 5 the emission of this product will have

nearly the same spectral distribution as pure $BaWO_4$, the incorporation of lead only causing a slight improvement of

Fig. 25. Spectral distribution of the reflection and the emission of tungstates at —180° C. The curves are marked by the symbols of the metallic ions, the suffixes indicating the number of these ions present per tungsten ion (for instance *Na* stands for $Na_2W_2O_7$, Sr_2 for Sr_2WO_5, etc.).

the temperature dependence and so presenting the possibility of observing it at —180° C.

The absorption edges were also determined photographically by measuring the reflections; the position of the absorption edge was defined arbitrarily as the point where a reflection of 10% was found.
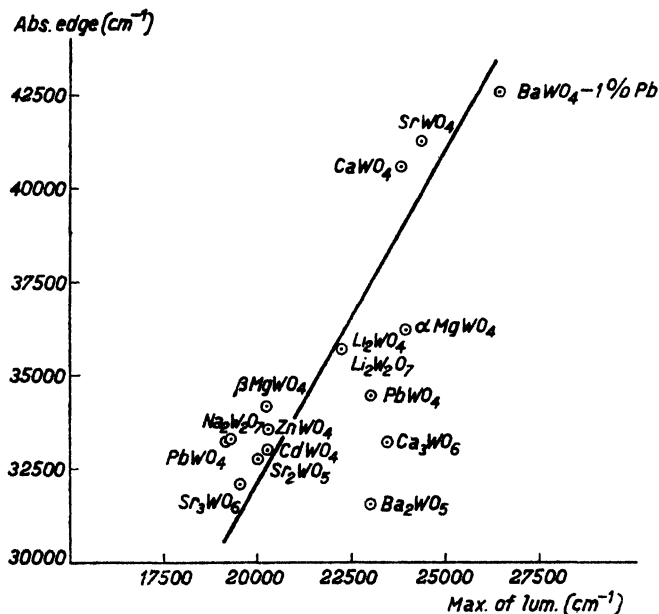
Fig. 25A. Correlation between the position of the absorption edge and the maximum of the emission for tungstates.

In Fig. 25 and Fig. 26 we give the results of our measurements with tungstates and molybdates respectively. Our emission data for the tungstates are in agreement with those to be found in literature (cf. Table III, List 28). For the molybdates, however, our results differ markedly from those of the literature, especially those of SCHLOEMER (cf. Table III, List 14). Only for $CaMoO_4$ do all observations agree. Yet we are convinced that our results are correct. Our results for the absorption edges of the molybdates are in good agreement with the

observations of SOUBAREW–CHATELAIN (*loc. cit.*). In Table

Fig. 26. Spectral distribution of the reflection and the emission of molybdates at —180° C.

XII and XIII we give the positions of the absorption edges and the maxima of emission for the various products.

Evidently a relation between absorption and emission xeists: substances showing an absorption extending to long wave lengths, emit in a band situated equally at a long wave-length position, and conversely. The phenomena in systems showing more than one emission with separated excitation regions, as already mentioned for $PbWO_4$, are especially
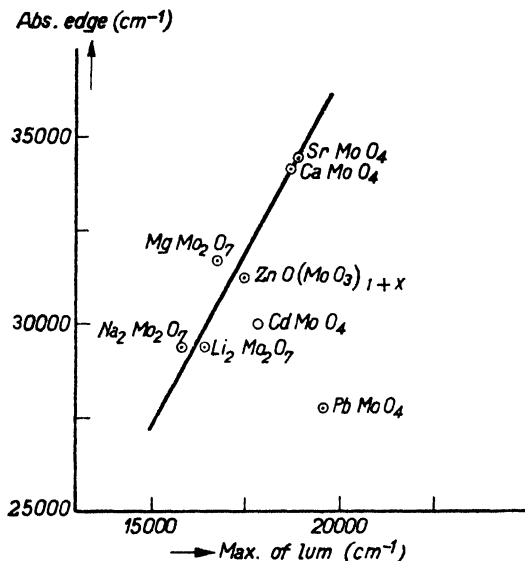
Fig. 26A. Correlation between the position of the absorption edge and the maximum of the emission for molybdates.

convincing. In Section 5 we shall find further material with the mixed crystals of $PbWO_4$ with $BaWO_4$, $SrWO_4$ and $CaWO_4$. In Fig. 25A and 26A we have plotted the position of the absorption edge against that of the emission maximum; the figures reveal the existence of a correlation such as that stated above.

The absorption and excitation bands on one side and the emission bands on the other side must be closely connected, both probably originating in one and the same configuration

of atoms. Because of the fact that the absorption is comparatively invariant, not only with changes in the chemical composition, but also with changes in the state of aggregation (crystalline state, solutions, cf. Section 1), the configuration responsible for both absorption and emission must be a constituent common to all the various systems, obviously *W* and *Mo* together with adjacent oxygen ions.

The gap occurring between absorption and emission may be due to the rather complicated structure of the "centres": after excitation the configuration may regroup, causing a considerable lowering of the excited levels and accordingly an emission shifted towards longer wave-lengths (Franck-Condon). It may also be, however, that the fluorescence is a transition from a high excited state, reached by the excitation, to a lower excited state. In this case we must expect an absorption in the infra red corresponding to the direct transition from the ground state to the low excited state.

In Table XII and XIII we have characterized the shift by the differences in position between the absorption edges and the emission maxima, measured in reciprocal centimeters. They are nearly constant, but show a slight tendency to increase for decreasing wave-lengths, i.e. for electronic transitions between widely separated levels. Considering the uncertainty due to this shift in addition to that caused by the width of the absorption and emission bands, the relation between absorption and emission seems to be satisfactorily proved by Fig. 25A and 26A, with the exception of a few outstanding discrepancies.

The deviating points (Ba_2WO_5 and Ca_3WO_6 in Fig. 25A, $PbMoO_4$ in Fig. 26A) may be explained by assuming that in these cases the absorption edges are not determined by the tungstate or molybdate absorptions, but by an absorption of some other kind, for instance one of the fundamental type corresponding to electronic transitions from (*W–O*), (*Mo–O*) or simple O^{2-} to the metallic ions. In accordance with this view, $PbMoO_4$ is blackened by the separation of lead upon irradiation into the absorption system ($\lambda < 3600$ Å). This

fact could not be understood if the absorption was due to an electronic transition within the MoO_4 radical.

4. THE TEMPERATURE DEPENDENCE OF THE EMISSION

As may be seen in Table XII and XIII, only a small number of tungstates and molybdates show luminescence at room temperature and their intensities vary considerably. In all
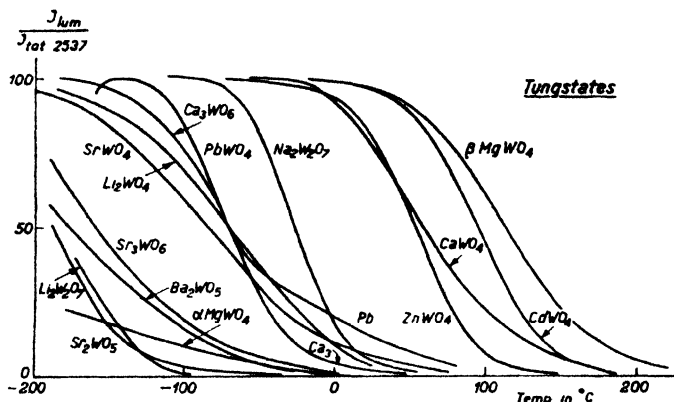
Fig. 27. Temperature dependence of the intensity of luminescence of the tungstates upon excitation by λ 2537 Å.

cases the faint emissions grow stronger at lower temperatures, whereas most of the non-luminescent products become luminescent at temperatures as low as —180° C. The few substances showing no luminescence even at —180°, ($BaWO_4$, Na_2WO_4, $BaMoO_4$, Na_2MoO_4) probably must be expected to become luminescent at still lower temperatures.

In Fig. 27 and 28 the intensity of luminescence for excitation by λ 2537 Å is given as a function of the temperature. The units in which the intensity is expressed are arbitrary, the maxima of the curves being adjusted to 100. In those cases in which the maximum intensity is not yet reached at —180° C the curves were adjusted either by fixing the inflection point at about 50, or by taking into account the relative intensities. In spite of these uncertainties, the curves give a proper picture

of the situation, probably even representing the true intensity relations between the emissions of the various substances,
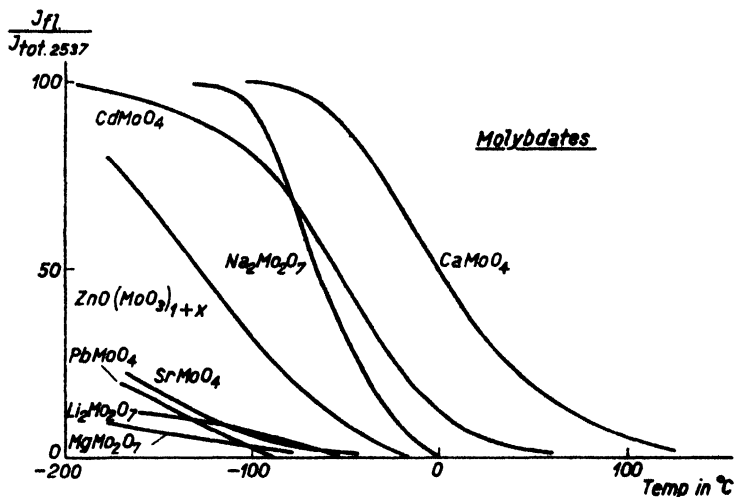
Fig. 28. Temperature dependence of the intensity of luminescence of the molybdates upon excitation by λ 2537 Å.

for although the maxima were fixed arbitrarily to 100, this may well correspond to reality. Indeed, measurements of the quantum efficiency of $CaWO_4$ and $SrWO_4$ showed the maximum effects to be equal for these two substances, both being approximately 90%.

All curves show a shape as frequently found for the temperature dependence (cf. Chapter VI). They consist of a flat part in the low temperature region and an adjoining S-shaped part in the upper temperature regions[1]. Only with $PbWO_4$ are some irregularities found. As we saw already in the previous section that $PbWO_4$ shows two different emission bands, a green and a blue one, the complicated curve observed must be a superposition of two curves, each giving the temperature

[1] A decrease towards low temperatures, as reported by DINGER and KUNERTH, *Iowa State College J. Sci.*, **14** (1940) **195**, was not observed.

dependence of one of the emission bands. Indeed, upon cooling we observe a gradual change in the colour of luminescence from green at room temperature to blue at temperatures below —80° C.

The temperature dependence of $CaWO_4$ is independent of the method of excitation (ultra violet, cathode rays) and is also the same for different intensities of the exciting radiation [1]. Different samples, however, may show differences in behaviour owing to differences in the perfection of the crystals. Badly crystallized products are only luminescent at low temperatures. This explains the fact that freshly precipitated $CaWO_4$ is non-luminescent at room temperature [2]. When the product is heated at a high temperature, or even when it is kept long enough at room temperature, the crystals grow more perfect and the quenching range rapidly approaches a limit. Therefore with normally prepared $CaWO_4$ luminophors always the same quenching range is found. The same was observed with other tungstates and with molybdates [3].

Within the groups of tungstates and molybdates great differences in quenching ranges occur, both groups covering a considerable temperature range. Substances with identical crystal structures show a systematic variation of the quenching temperature with the atomic number of the cations. Series of this kind are formed by the compounds of *Ba–Sr–Ca* crystallizing in the scheelite structure, and of *Mg–Zn–Cd* crystallizing in the wolframite structure. Comparing corresponding tungstates and molybdates of the same crystal structures, the luminescence of the tungstates is somewhat more persistent than that of the molybdates (a difference of 100—200° C).

5. MIXED CRYSTALS OF $PbWO_4$ WITH $CaWO_4$, $SrWO_4$ AND $BaWO_4$

Using a procedure completely analogous to that described in Section 2, we have prepared mixed crystals of the binary

[1] cf. also E. A. Ab, *Bull. acad. sci.* U.R.S.S. (sér. phys.), **9** (1945) 467.
H. W. Leverenz, *R.C.A. Review*, **7** (1946) 199.

[2] E. Tiede–A. Schleede, *Z. Elektrochem.*, **29** (1923) 305.

[3] F. A. Kröger, *Philips Res. Rep.*, **2** (1947) 340.

systems $PbWO_4$–$CaWO_4$, $PbWO_4$–$SrWO_4$ and $PbWO_4$–$BaWO_4$.

Since $PbWO_4$, $CaWO_4$, $SrWO_4$ and $BaWO_4$ all show the same crystal structure, the scheelite-structure, with only slight differences in lattice dimensions (cf. Table XIV), the formation

TABLE XIV

SCHEELITE STRUCTURES

Substance	*a*	*c*	Substance	*a*	*c*
$CaWO_4$	5.25	11.35	$CaMoO_4$	5.23	11.44
$SrWO_4$	5.40	11.90	$SrMoO_4$	5.37	11.95
$BaWO_4$	5.60	12.70	$BaMoO_4$	5.56	12.76
$PbWO_4$	5.44	12.01	$PbMoO_4$	5.41	12.08

Data according to Struktur Berichte 1913–1932

of solid solutions must be expected to occur to a large extent. This indeed was found: for the systems containing compounds of *Ca* and *Ba* as components, *X*-ray diffraction photographs proved the existence of a homogeneous series of mixed crystals [1]. For the systems containing strontium this method cannot be used, because of the great resemblance in cell-dimensions between $PbWO_4$ and $SrWO_4$. By analogy it seems permissible to conclude that a homogeneous series occurs here too.

The absorption, excitation, and emission of the mixed crystals have been studied in order to find out how these properties varied with the composition.

In Fig. 29 the reflection curves are given for various compositions. In principle, the reflection varies similarly with the composition in all three systems $CaWO_4$–$PbWO_4$, $SrWO_4$–$PbWO_4$ and $BaWO_4$–$PbWO_4$. In addition to absorption bands of $CaWO_4$, $SrWO_4$ or $BaWO_4$, the incorporation of 0.1 mol % $PbWO_4$ causes the occurrence of an absorption band extending to longer wave-lengths. On increasing the lead content of the mixed crystals the latter absorption increases; the reflection curves vary continuously between the products with a low lead content and pure $PbWO_4$.

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[1] So far, formation of solid solutions was only proved for $CaWO_4$ containing a few percents of $PbWO_4$; H. G. JENKINGS-A. H. MC KEAG-H. P. ROOKSBY, *Nature*, **143** (1939) 978.
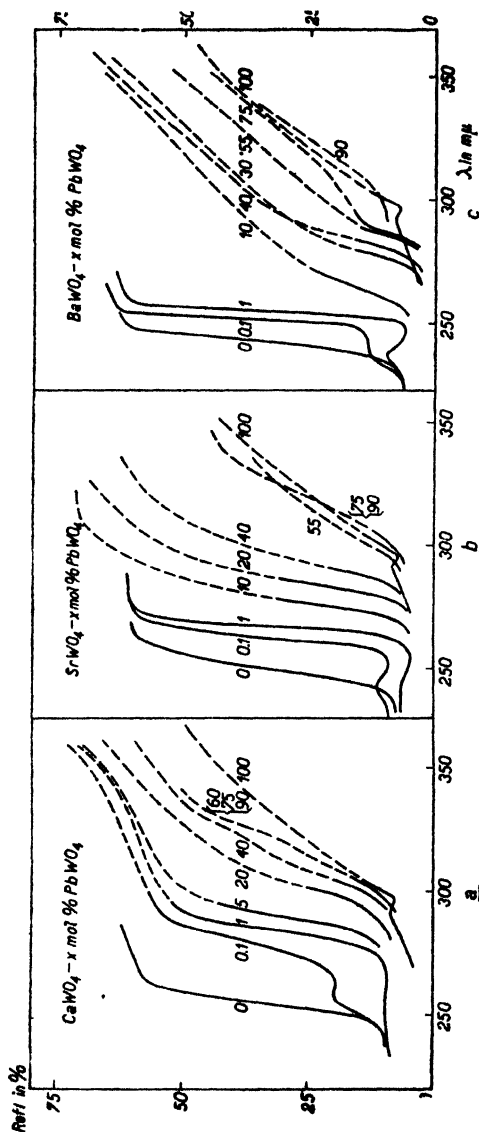
Fig. 29. Spectral distribution of the reflection of solid solutions of:
a. $CaWO_4$ – *x* mol % $PbWO_4$
b. $SrWO_4$ – *x* mol % $PbWO_4$
c. $BaWO_4$ – *x* mol % $PbWO_4$
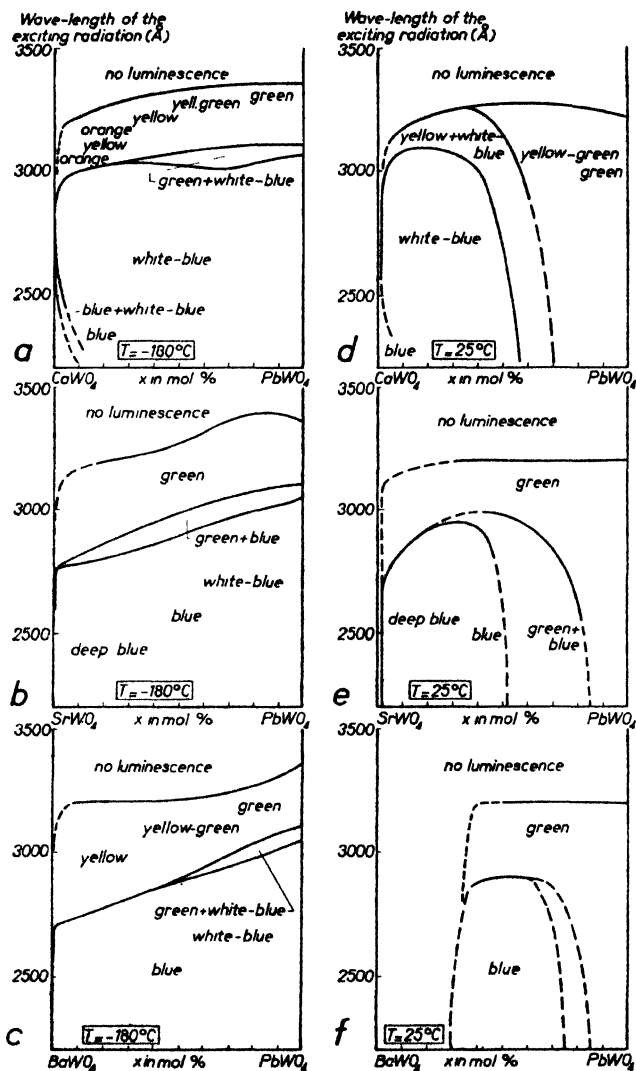
Fig. 30. A survey of the excitation in the systems $CaWO_4$–$PbWO_4$, $SrWO_4$–$PbWO_4$ and $BaWO_4$–$PbWO_4$ at —180° C (*a*, *b*, *c*) and room temperature (*d*, *e*, *f*).

In the new absorption, correlated with lead, we must distinguish between two parts. The first and most important part, limited at the long wave-length side by a fairly sharp edge, shows the strongest absorption; photographs revealed a fine structure in the neighbourhood of the absorption edge, especially for $BaWO_4$-1 mol % *Pb*. In the second part the absorption is considerably fainter. The band extends to longer wavelengths and is much less defined; it is found as a long wave-length extension of the first part. In Fig. 29 those parts of the reflection curves which correspond to this second absorption are given by dotted lines.

Irradiation into the three different parts of the absorption spectrum gives rise to luminescence in different emission bands. Fig. 30 shows the spectral distribution of the excitation as a function of the composition at room temperature and at —180° C.

At —180°, the situation is the least complicated (Fig. 30 *a*, *b* and *c*). Irradiation into a short wave-length region, the long-wave limit of which varies from 2700 to 3100 Å depending on the composition, causes luminescence chiefly in the blue or near ultra violet [1]. Excitation in a region at longer

TABLE XV
RELATIVE INTENSITIES
(EXCITATION BY λ 2537 AND λ 3130)

mol % $PbWO_4$	$CaWO_4$–$PbWO_4$		$SrWO_4$–$PbWO_4$		$BaWO_4$–$PbWO_4$	
	blue fl.	green fl.	blue fl.	green fl.	blue fl.	green fl.
1					27	
10			182			
20	120	26	170		82	
30			170			
40	117	52.5	154	20	118	
55	92	82	104	35	86	8
75	89	130	87	96	71	27
90	99	126	91		82	73
100	100	100	100	100	100	100

[1] Particularities of the excitation in this region will be discussed furtheron.

wave-lengths gives rise to an emission varying from green to orange. In an intermediate zone blue and green emissions occur simultaneously. If we compare these excitation spectra with the absorption spectra described above, the blue emissions are obviously excited in the well defined absorption bands (drawn in full lines in Fig. 29) and the green-orange luminescence in the badly defined "tail" absorption (dotted in Fig. 29).

In Table XV we give the intensities of the blue emission at —180° C excited by λ 2537 Å and of the green emission excited by λ 3130 Å; all in arbitrary units and hence only to be used to indicate the relative magnitude. They were measured by means of a rough quantitative photographic method and we do not claim them to be very accurate.

The blue emissions are of the same order of intensity over all systems. Only in products of the system $BaWO_4$–$PbWO_4$ with a high barium content does the temperature quenching reduce the intensity (cf. Fig. 31*c*: the maximum intensity is not yet reached at —180° C). The intensities of the long wave-length emissions diminish with decreasing lead content. The systems containing less than 5 mol % *Pb* do not show this emission at all.

An increase of temperature causes quenching of all kinds of emission in the normal way. In Fig. 31, *a*, *b* and *c* we give the temperature dependence of the short wave-length emission (excitation by λ 2537) as a function of the composition in the three systems. The numbers at the curves refer to the lead content in mol percents. Where green emissions occurred at higher temperatures, the blue bands were measured through a blue filter.

The temperature dependence proves to be a function of the composition, but does not change continuously with it. This may be shown especially clearly by considering the quenching ranges (Fig. 32 *a*, *b* and *c*)[1]. Because of the fact that these ranges are characteristic of a certain emission in a lattice[2], the discontinuous variation proves that the observed emission is

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[1] For a definition of the quenching ranges cf. Chapter VI, Section 2.12.

[2] This is made probable in Chapter VI.
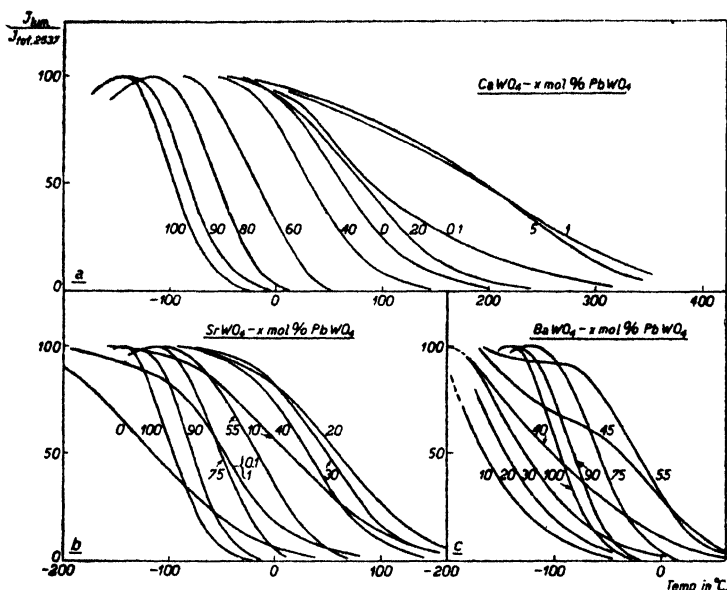
Fig. 31. Temperature dependence of the blue emissions of:
a. $CaWO_4$ – x mol % $PbWO_4$
b. $SrWO_4$ – x mol % $PbWO_4$
c. $BaWO_4$ – x mol % $PbWO_4$
upon excitation by λ 2537 Å.

not a single band, varying continously from $CaWO_4$, $SrWO_4$ or $BaWO_4$ to $PbWO_4$, but a superposition of several bands, each becoming important in a certain composition range. Actually all phenomena can be explained by the assumption of three bands, to be referred to as I, II and III. I indicates the band occurring with pure $PbWO_4$, III indicates the band occurring with pure $CaWO_4$, $SrWO_4$ and $BaWO_4$, whereas band II is only found with mixed crystals.

For each band the quenching range varies slightly with the composition. In those cases where an extremely broad quenching range is observed (e.g., $SrWO_4$–40 mol % $PbWO_4$), we have to consider two superposed bands.

The effects pointing to the existence of three emission bands are clearest in the system $BaWO_4$–$PbWO_4$. The ultra violet
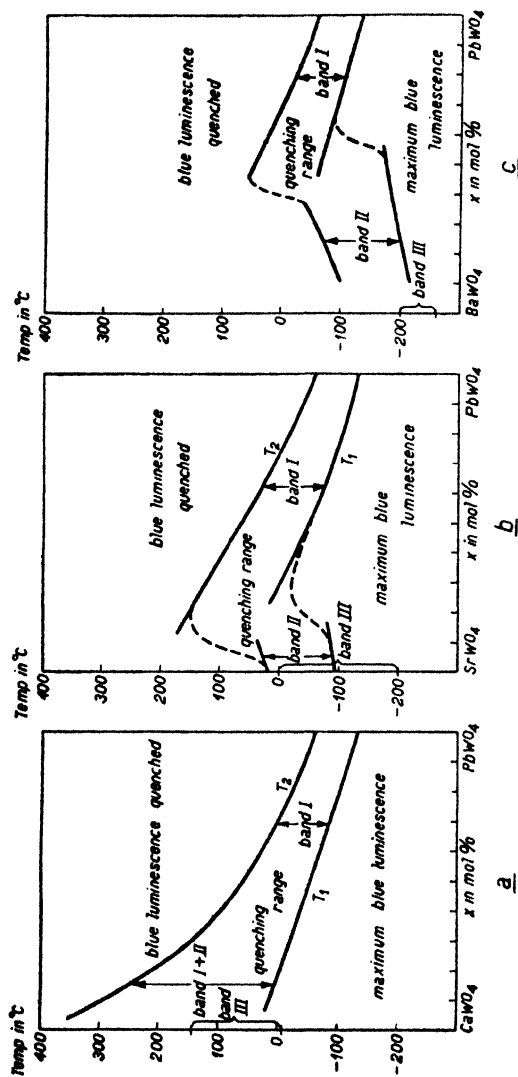
Fig. 32. Quenching ranges of the blue emissions of
a. $CaWO_4 - x$ mol % $PbWO_4$
b. $SrWO_4 - x$ mol % $PbWO_4$
c. $BaWO_4 - x$ mol % $PbWO_4$

band III to be found with pure $BaWO_4$ probably below —180° C, is already observable above —180° in products containing a small amount of $PbWO_4$. Band II predominantly determines the temperature dependence between 10 and 50 mol % $PbWO_4$, while band I is predominant above 50 mol % $PbWO_4$. With $SrWO_4$–$PbWO_4$ we already find indications for band II between 1 and 10 mol % $PbWO_4$ and I is dominant between 15 and 100 mol % *Pb*. Finally with $CaWO_4$–$PbWO_4$ III is found with pure $CaWO_4$, I predominates over nearly the entire composition range; while only the broad quenching range of $CaWO_4$–0.1/1 mol % $PbWO_4$ indicates that a mixture of I, II and III occurs here. The composition region in which band II is indicated by the intensity-temperature curves, is shifted towards low lead contents in the sequence *Ba–Sr–Ca*.

All the effects described above are highly dependent on the wave-length of the radiation used for excitation, qualitatively as well as quantitatively. Differences between excitation into the well defined absorption regions and the badly defined tail absorption have already been discussed in connection with Fig. 30, *a*, *b* and *c*: excitation into the first regions gives rise to a blue emission, into the latter regions to a green emission. However, differences also occur over the short wave-length region, depending on whether we irradiate into the absorption bands of $CaWO_4$, $SrWO_4$ or $BaWO_4$ or into the bands which must be correlated with lead. Irradiating for instance $CaWO_4$–1 mol % $PbWO_4$ with ultra violet of a wave-length falling in the absorption region of $CaWO_4$ (e.g., 2400 Å), we observe emission III exclusively. Excitation with a wave-length falling in the well-defined extra absorption (e.g., 2700 Å) gives rise to the emission of bands I+II. In the intermediate region we observe I, II and III superposed.

A systematic investigation of the temperature dependence of the green–orange emission, raised by excitation with λ 3130 Å, has not been carried out. In all cases rough measurements showed a temperature quenching of the same type as that occurring with the short wave-length emission. The green-orange emission bands are quenched at a slightly higher
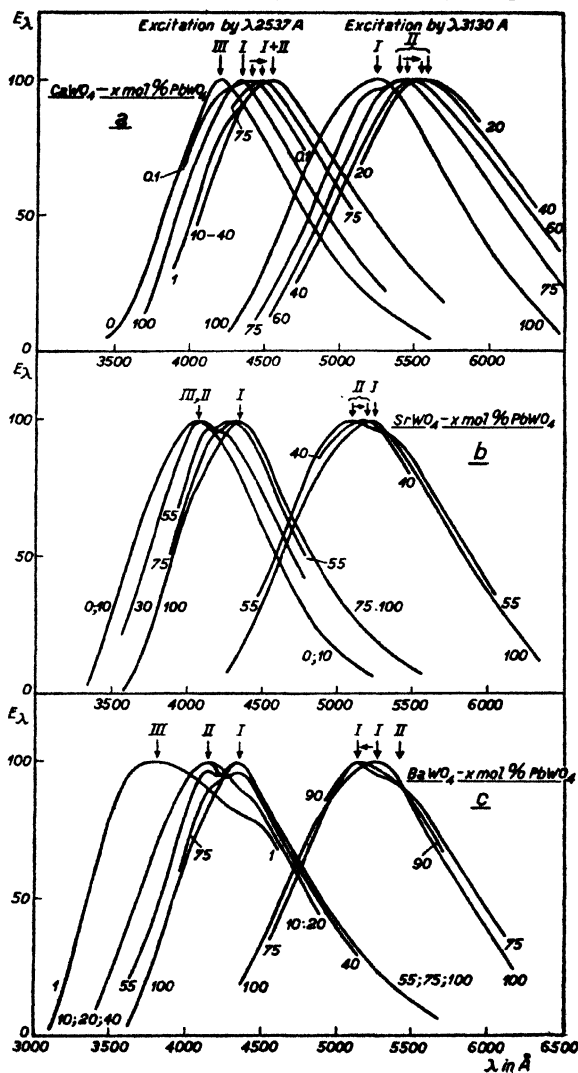
Fig. 33. Spectral distributions of the emissions of
a. $CaWO_4 - x$ mol % $PbWO_4$
b. $SrWO_4 - x$ mol % $PbWO_4$
c. $BaWO_4 - x$ mol % $PbWO_4$
excited by λ 2537 Å and λ 3130 Å at —180° C.

temperature than the blue bands. (Cf. the behaviour of $PbWO_4$, Section 4).

The spectral distribution of the emissions at —180° C has been measured for the short wave-length emission excited by λ 2537 Å, as well as for the long wave-length emissions excited by λ 3130 Å. In Fig. 33, *a, b* and *c* the bands are seen to show a structure, indicating the existence of several sub-bands. A unique separation into sub-bands presents difficulties, especially in certain cases where no separate maxima are to be observed. Yet, in accordance with the results obtained above, the structure of the short wave-length emissions can be fully explained by the assumption of three sub-bands (I, II and III). The long wave-length bands only show evidence for the existence of two sub-bands. Considering that the green emission is only found in the presence of lead and does not occur in the pure tungstates of barium, strontium and calcium, obviously the missing band is that of type III and accordingly the bands found must be denominated I and II.

The existence of three sub-bands having thus been made probable, we can occupy ourselves with the attribution of these bands to certain tungstate groups. It seems acceptable to relate band I with tungstate groups surrounded by lead ions exclusively, band III to tungstate groups surrounded by either barium, strontium or calcium ions and II, finally, to tungstate groups with a mixed surrounding.

As regards the origin of the three short wave-length bands in relation to that of the two long wave-length bands, two possibilities exist. In the first possibility, the bands are related pairwise: I–I, II–II, III–. . ., each pair corresponding to two different electronic transitions in one kind of tungstate group. It might also be possible, however, that each kind of emission arises from differently placed groups: the blue bands in normal groups, the green bands in perturbed groups in the neighbourhood of lattice flaws. Conclusive argument in favour of one of these situations cannot yet be given.

Returning with our present knowledge to the description of the distribution of the excitation, it is not difficult to understand the situation at room temperature (Fig. 30, *d, e, f*). In

the system $CaWO_4$–$PbWO_4$ blue bands occur with the products of high and medium calcium content. In the system $SrWO_4$–$PbWO_4$, the blue emissions in the corresponding composition regions are much weaker, whereas in the system $BaWO_4$–$PbWO_4$ an extremely faint blue luminescence remains ob-
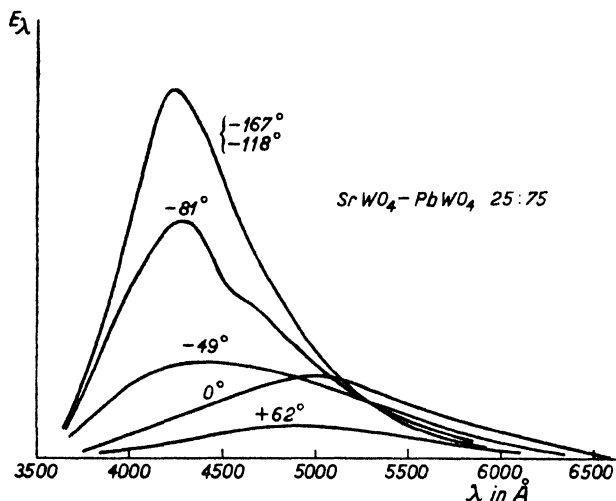
Fig. 34. Spectral distribution of the luminescence of $SrWO_4$ – 75 mol % $PbWO_4$ for excitation by λ 2537 at various temperatures (true intensity ratios).

servable only in the central composition region. The products on the lead side of the systems all behave nearly identically, as must be expected in view of the low concentration of *Ca*, *Sr* and *Ba* in this region. The blue emission is quenched; a green luminescence, observed with the other products only upon excitation in the long-wave region of the absorption, appears here over the whole excitation spectrum. Hence when a product of this composition is heated from —180° C up to room temperature, the luminescence, excited by some radiation with a wave-length shorter than 2900 Å, starts as blue, but in a certain temperature region gradually changes into green.

We have studied this colour change quantitatively in order to see whether the green band is substituted for the blue band or whether it is also emitted at low temperatures, but is then dominated by the blue band. In Fig. 34, we give the results of our photographic measurements on $SrWO_4$–75 mol % $PbWO_4$, excited by λ 2537 Å. It shows the correct relative intensities of the emission in the various spectral regions for —167°, —118°, —81°, —49°, 0° and 62° C. A separation of the total emission into two sub-bands, a blue one and a green one is not very well possible, yet the increase of the intensity in the region above 5000 Å towards higher temperatures proves that the green band is growing, though always remaining considerably fainter than the original blue band. At 0° C the green band is probably nearly "pure"; the total energy emitted then amounts to 40% of that of the emission at low temperatures (—167°). This result is extremely noteworthy. A simple explanation which might be proposed, the attribution of the effect to a variation in the absorption conditions of the two bands, does not hold: as a short-wave absorption region is correlated with the blue emission and a faint long-wave absorption with the green emission (cf. Fig. 34), on increasing the temperature the first absorption must be expected to extend to longer wave-lengths, covering the faint absorption to a greater extent, and hence having an exactly opposite effect upon the emission to that observed. Hence we are forced to assume that energy used for the emission of the blue band at low temperatures, is partly transferred, after the quenching of this band, to the system responsible for luminescence in the green band.

Several patents exist which claim an improvement in the luminescent properties of $CaWO_4$ for excitation by ultra violet radiation or X-rays by the incorporation of a small quantity of $PbWO_4$[1]. The effect can be explained satisfactorily with the aid of our present knowledge. For the excitation by ultra violet, the lead sensitizes the tungstate by the presence

[1] W. A. Roberts, *U.S.A. Pat.* 2.132.273; *Brit. Pat. Spec.* 485.329; *Fr. pat.*, 820.886.
A. H. McKeag, *Brit. Pat. Spec.* 485.875; *D.R. Pat.* 666.086.

of the extra absorption band at the long wave-length end of the $CaWO_4$ absorption; the excitation region being extended from 2600 to 3000 Å [1]. In the second place — and this effect applies also to the luminescence excited by other methods — an emission of slightly different spectral distribution occurs which is more persistent with respect to temperature quenching. For pure $CaWO_4$ the efficiency at room temperature is already below the maximum value, falling rapidly with increasing temperature. Due to the smaller slope of its intensity-temperature curve, $CaWO_4$–Pb starts at room temperature with a higher efficiency, which furthermore decreases less with temperature (cf. Fig. 31*a*). The last factor is especially important in engineering, because in most cases where a luminophor is used, the working temperature is above room temperature.

We have also studied the system $CaMoO_4$–$PbMoO_4$ [2]; here the situation is much like that in the tungstate system.

6. MIXED CRYSTALS $CaWO_4$–$CaMoO_4$

$CaWO_4$ and $CaMoO_4$ both crystallise in the scheelite structure and have nearly identical cell-dimensions (cf. Table XV). Although, just because of this great similarity, the occurrence of mixed crystals cannot be proved by means of *X*-ray diffraction — as was mentioned in Section 5 for $SrWO_4$–$PbWO_4$ — yet it seems safe to assume the existence of a continuous series of solid solutions. Such solid solutions are known as minerals, and are called scheelite if the amount of molybdenum is below 50%, powellite if it is above 50%.

Optically the solid solutions behave as ideal mixtures of $CaWO_4$ and $CaMoO_4$. The spectral distributions of absorption, excitation and emission are a superposition of the bands of the components [3].

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[1] The excitation limit of $\sim$3000 Å for $CaWO_4$–1% Pb was also observed by C. G. FOUND, *Trans. Illum. Eng. Soc.*, **34** (1938) 161. However R. P. JOHNSON, *Am. J. Phys.*, **8** (1940) 143 and N. C. BEESE, *J.O.S.A.*, **29** (1939) 278 report the same for $CaWO_4$: apparently they have also been working with $CaWO_4$–Pb.

[2] F. A. KRÖGER, *Philips Res. Rep.*, **2** (1947) 183.

[3] The same was observed for the emission by M. SERVIGNE, *C.R. Paris*, **210** (1940) 440 and R. GREENWOOD, *Econ. Geol.*, **38** (1934) 56. cf. also T. S. WARREN, *The Mines Magazine*, July 1944, p. 343.
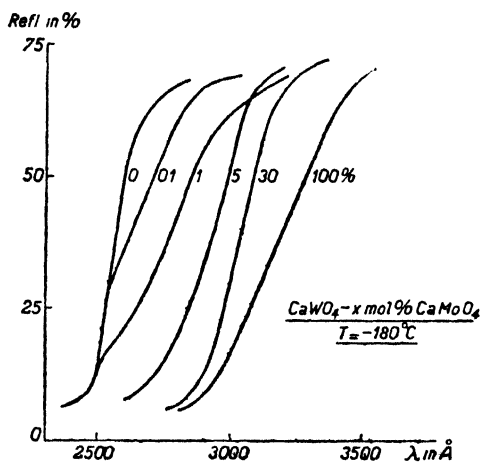
Fig. 35. Reflection of mixed crystals $CaWO_4$–$CaMoO_4$ at —180° C.
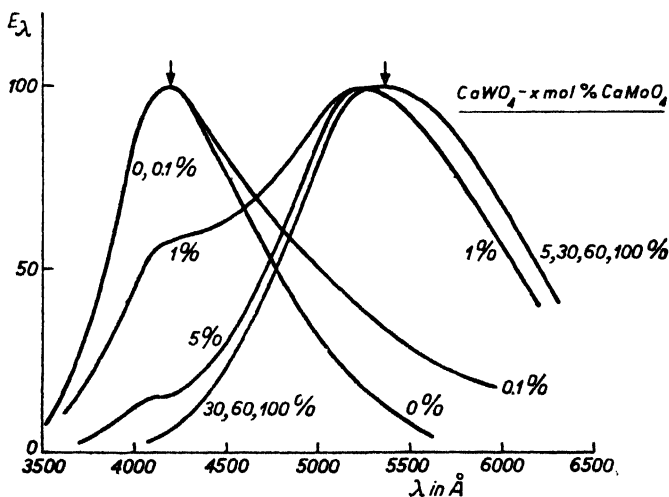
Fig. 36. Spectral distribution of the emission of mixed crystals $CaWO_4$–$CaMoO_4$ for excitation by λ 2537 Å at —180° C.

In Fig. 35 we give the reflection spectra at —180° C for mixed crystals of various compositions. Fig. 36 shows the spectral distribution of the emission on excitation by λ 2537 Å also at —180° C. The figures by the curves refer to the concentration of molybdate in mol percents.

Excitation occurs for each emission in its own absorption band: the tungstate emission is raised with $\lambda < 2600$ Å, the molybdate emission with $\lambda < 3400$ Å. The molybdate band is only to be obtained completely pure upon excitation with $2600 < \lambda < 3400$ into that part of the molybdate absorption band not coinciding with the tungstate absorption. Excitation in the region $\lambda < 2600$ Å produces both emission bands simultaneously in proportions dependent on the relative magnitude of the partial absorption coefficients as well as on the efficiencies of the two luminescence processes. The first factor, determining the fraction of the exciting radiation which is absorbed in the tungstate and molybdate absorption bands respectively, is a function of the composition of the mixed crystals and of the wave-length of the irradiating light. The second factor determines the fraction of the radiation, absorbed in each band which is converted into luminescence and it is obviously a function of the temperature.

For excitation in a region where both absorptions are of the same order of magnitude, and at a temperature low enough to eliminate temperature quenching, the two emissions are emitted in proportion to the relative concentration of tungstate and molybdate in the solid solution. This is the case for excitation by radiation of a short wave-length and also for excitation by X-rays or β-rays. When, however, the exciting radiation is absorbed much more strongly in one band than in the other, the first emission is correspondingly at an advantage. This is realized on irradiation with λ 2537 Å which, being situated near the absorption edge of $CaWO_4$, is absorbed much more strongly in the molybdate absorption band than in the tungstate band. Accordingly even for comparatively low molybdate concentrations ($\sim$ 1 mol %) the molybdate emission is predominant (cf. Fig. 36).

The temperature dependence of the separate emissions is nearly

constant over the entire composition range, remaining practically identical with those of the corresponding pure components.

We have also studied the systems $Zn(W\text{-}Mo)O_4$ and $Mg(W\text{-}Mo)O_4$; tungstates and molybdates have their own absorption and emission bands also in these cases, but the situation is complicated by the occurrence of several different crystal structures [1].

7. THE DECREASE OF LUMINESCENCE OF THE TUNGSTATES UNDER THE INFLUENCE OF FOREIGN IONS AND ITS CONSEQUENCES WITH REGARD TO THE CENTRES OF LUMINESCENCE

7.1 Introduction

In Section 3 of this chapter we have seen that all tungstates and molybdates show absorption bands in the near ultra violet which must probably be attributed to electronic transitions within tungsten-oxygen or molybdenum-oxygen configurations. Upon absorption of ultra violet radiation in these absorption bands, electrons may be excited in all tungstate or molybdate groups all over the lattice. As it was shown in the same paragraph that a close relationship exists between the absorption bands and the emission bands, it seemed tempting to correlate the emission equally with the tungstate and molybdate groups.

Within the frame-work of this assumption two possibilities remain open: either all tungstate or molybdate groups are able to give rise to luminescence or only distinct groups — for instance distorted ones in the neighbourhood of lattice flaws, or ions present in excess above the stoechiometric composition — are centres of luminescence. According to RIEHL [2], observations by TIEN-HUAN TSAO [3] favour the latter possibility. The latter author found that the luminescence of $CaWO_4$ upon excitation by X-rays was practically totally quenched by the presence of $\frac{1}{27}$ mol % chromium or $\frac{1}{9}$ mol % manganese. If all tungstate groups were capable of acting as centres of lumines-

[1] F. A. KRÖGER, *Philips Res. Rep.*, **2** (1947) 177.
[2] N. RIEHL, *Ann. Phys.*, (5), **29** (1937) 661; *Physik und Anw. der Luminescenz*, Berlin **1941**, p. 37/38.
[3] TIEN-HUAN TSAO, *Dissertation* Greifswald **1939**.

cence, the strong effect observed for such a relatively low content of contaminating ions would not be easy to explain. Assuming, however, that but a few centres of luminescence are present in the lattice, the contaminating ions could play a part similar to that of the "killers" in zinc-sulphide luminophors.

MARDEN and MEISTER [1], however, studying the diminishing effects of a number of foreign ions upon the intensity of luminescence in $CaWO_4$ excited by ultra violet radiation of λ 2537 Å, observed much smaller effects: 1% manganese only caused a decrease of the intensity to 45%, whereas for $MgWO_4$ the effects were even far less pronounced.

Since consistent experimental material could make the determination of the nature of the centres of emission possible, we have repeated some of the experiments and carried through some new ones.

7.2 Experimental part

$CaWO_4$ and $MgWO_4$, pure and with addition of 0.001, 0.01, 0.1 and 1 mol % of several ions foreign to the lattice, were

TABLE XVI

APPROXIMATE INTENSITY OF THE LUMINESCENCE FOR CONTAMINATED $CaWO_4$ IN % OF THAT FOR PURE $CaWO_4$; EXCITATION BY λ 2537 Å

Added ions:	0.001 mol %	0.01 mol %	0.1 mol%	1 mol %	Colour of $CaWO_4$-1% X
Cr	95	66	28	1.3	yellow
Fe	98	92	77.5	39.6	brown-violet
Mn	91	81.5	63.3	43	greyish
Ag	98.5	100	72.5	53	sl. brownish
Ni	96.5	100	91.5	69	sl. greenish
Co	93	97	85	68	sl. blueish
Ti	100	93.5	86	75	white
Cu	—	96.5	93	79.5	
Sn	99	91	90	83	white
Sb	95	92	100	103	white
Zr	95	95.5	99	98	white
Th	100	98.5	87.5	94	white
Al	98	100	90	100	white

[1] J. W. MARDEN–G. MEISTER, *Trans. Illum. Eng. Soc.*, **34** **(1939) 503.**

made by the method described in Section 2 of this chapter. The ions incorporated in $CaWO_4$ were aluminium, tin, copper, titanium, nickel, cobalt, iron, chromium, manganese, silver, antimony, zirconium, and thorium. $MgWO_4$ was prepared only with an addition of manganese.

The intensity of luminescence upon excitation by λ 2537 Å was measured by means of a barrier-layer photo-cell, the sensitivity of which was dependent on the wave-length. As
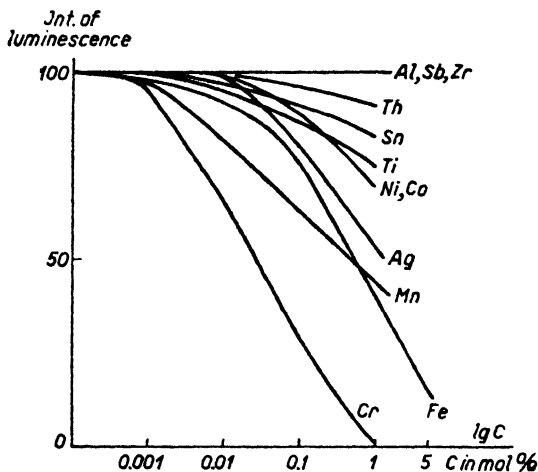
Fig. 37. The intensity of the luminescence of $CaWO_4$ containing various foreign ions, as a function of the concentration of these ions (excitation by λ 2537 Å).

we did not account for variations in the spectral distribution of the luminescence, the measured voltage will not be quite proportional to the intensity of the luminescence; yet the results are satisfactory to provide a rough picture of the quenching power of the different contaminations. In Table XVI we have compiled the values obtained for the intensity of the luminescence relative to pure $CaWO_4$ [1]

[1] The quenching proves to be nearly independent of the temperature: the shape and the position of the intensity-temperature are not changed.

together with the colour of the products containing one mol per cent of contaminating ions. In Fig. 37 these values are represented graphically. The results are in perfect agreement with those obtained by MARDEN and MEISTER (*loc. cit*).

It is remarkable that those added ions cause the strongest diminishing effect upon the luminescence, which colour most deeply the crystals in which they are embedded
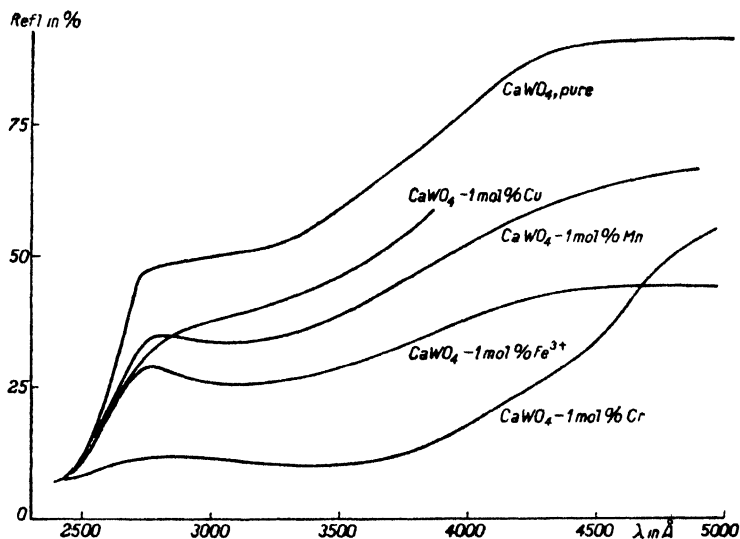
Fig. 38. Reflection spectrum of $CaWO_4$, pure and containing 1 mol % *Cu*, *Mn*, *Fe* or *Cr*, at room temperature.

(cf. Table XVI). Reflection measurements with $CaWO_4$, contaminated by copper, iron, chromium, and manganese reproduced in Fig. 38, show that this colouring is caused by an additional absorption band, occurring at the long wave-length side of the edge of the tungstate absorption. As irradiation into this extra absorption does not give rise to luminescence, a simple explanation for the process of quenching is suggested: for excitation by ultra violet radiation, the additional absorption subtracts a part of the exciting light, and

also absorbs a fraction of the luminescence raised by the effective absorption.

The first effect must be dependent on the relative magnitude of the coefficients of effective and ineffective absorption. When the effective tungstate absorption is strong with regard to the ineffective absorption due to the contaminations, the quenching will be only small. When, however, the tungstate absorption is of the same order or even fainter, the quenching will be considerable and may become nearly total. Both situations can be realized by making use of the fact that in the neighbourhood of the absorption edge of the tungstate, the effective absorption varies considerably within a comparatively narrow wave-length range [1].

The second cause, the absorption of the luminescence raised by the effectively absorbed part of the exciting radiation, is dependent not only on the absorption coefficient for the luminescence, but also on the absolute magnitude of the absorption coefficient for the exciting radiation. When the luminescence is observed from the side of the powder layer on which the exciting radiation is falling, the quenching effect due to the self-absorption is small if the luminescence is excited in a thin layer at the surface of the crystals, i.e., when the exciting radiation is absorbed strongly. Conversely, for a weak absorption of the exciting light, the luminescence is excited in a much greater depth, and has to traverse a longer path on its way out of the crystals and so will be reabsorbed to a much higher extent.

In order to test these views, we have measured the energy efficiency of luminescence on excitation in different parts of the absorption spectrum for certain systems in which the effective absorption varies strongly. With $CaWO_4$ (abs. edge ~2500 Å) these wave-lengths were 2483 Å, situated well into the absorption region, 2652 Å in the long-wave extension,

[1] Although we have no knowledge about the behaviour of the ineffective absorption in the wave-length region where it is submerged in the tungstate absorption, it seems highly improbable that the ineffective absorption should change to the same extent as the effective absorption in the neighbourhood of the edge of the latter.

and 2537 Å in the intermediate region. With $MgWO_4$ (abs. edge ~ 3000 Å) the corresponding wave-lengths were 2804, 2967 and 3130 Å.

TABLE XVII

RELATIVE EFFICIENCY q OF LUMINESCENCE, AND REFLECTION OF THE IRRADIATING LIGHT FOR CONTAMINATED $CaWO_4$
$q = \text{eff}/\text{eff } CaWO_4$

Added ions in mol %	2483 Å		2537 Å		2652 Å	
	Refl. 2483	q	Refl. 2537	q	Refl. 2652	q
0	16	100	20.5	100	50	100
0.001% *Fe*	16.6	90	20	93	44	82
0.01 ,,	18	103	22	90	48	90
0.1 ,,	21	80	20	72	53.5	67
1 ,,	13.5	47	15.6	37	32	17
0.001% *Cr*	18	88	22.5	95	47	88
0.01 ,,	20	69	24.5	71	49	51
0.1 ,,	11.7	25	19.4	14	33	8
0.01% *Cu*	24.5	97	29	95	55	90
0.1 ,,	21	102	27.5	91	53	94
1 ,,	11.6	97	28.5	92	48	87

Absorption edge for pure $CaWO_4$ ~ 2500 Å

TABLE XVIII

RELATIVE EFFICIENCY q OF LUMINESCENCE, AND REFLECTION OF THE IRRADIATING LIGHT FOR CONTAMINATED $MgWO_4$
$q = \text{eff}/\text{eff } MgWO_4$

Added ions in mol %	2804 Å		2967 Å		3130 Å	
	Refl. 2804	q	Refl. 2967	q	Refl. 3130	q
—	13	100	20	100	60	100
0.001% *Mn*	13.1	96	19.4	95	56.5	90
0.01 ,,	12.5	93	16.1	90	49.5	75
0.1 ,,	11.7	61	16.4	53	36.8	20
1 ,,	—	—	—	—	14.5	0.7

Absorption edge for pure $MgWO_4$ ~ 3000 Å

Table XVII shows the efficiency of luminescence and the, reflection of the exciting radiation for $CaWO_4$–*Fe*, *Cr* and *Cu*,

and Table XVIII for $MgWO_4$–Mn. We give the values of the efficiencies relative to the same value for the pure substances. In Fig. 39 the reflection of pure $CaWO_4$ and of $MgWO_4$ for
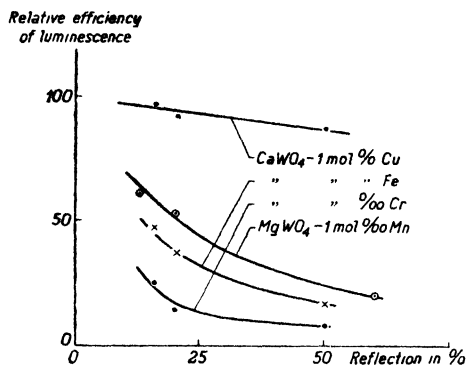
Fig. 39. Relative intensity of the luminescence as a function of the reflection of the exciting radiation by the uncontaminated compounds.
a. $CaWO_4$ – 1 mol % *Cu*
b. $CaWO_4$ – 1 mol % *Fe*
c. $CaWO_4$ – 1 mol ‰ *Cr*
d. $MgWO_4$– 1 mol ‰ *Mn.*

the three different wave-lengths are plotted against the quenching effected by one mol percent of added ions (data from Tables XVII and XVIII). The figure clearly reveals a correlation between the reflection — and hence also the absorption — of the exciting radiation and the quenching power of the contamination in the sense demanded by our theory: strong quenching for a strong ineffective absorption and a relatively weak effective absorption.

The small quenching effect found with $MgWO_4$ excited by λ 2537 Å, can now be explained: in contradistinction to $CaWO_4$, in which 2537 Å falls near to the absorption edge and is absorbed relatively weakly, in $MgWO_4$ 2537 Å falls into the tungstate absorption and is strongly absorbed; the luminescence is accordingly much less quenched.

For excitation by *X*-rays the absorption of the exciting

radiation will be influenced only to a negligible extent. In this case the re-absorption of the luminescence will exclusively determine the decrease of luminescence. Owing to the penetrating power of the *X*-rays, luminescence is generated practically homogeneously throughout the whole layer of crystals; luminescence has to cover on the average a long path through the crystals and accordingly a considerable quenching must be expected. Probably this accounts for the observation of TIEN–HUAN TSAO mentioned above.

The intensity of the luminescence of $CaWO_4$, pure and with the addition of chromium, iron, manganese, and copper, upon excitation by *X*-rays, was measured photographically. In accordance with our view, the luminescence is weakest in the cases where the absorption of the luminescent light

TABLE XIX

INTENSITY OF THE LUMINESCENCE OF CONTAMINATED $CaWO_4$ RELATIVE TO PURE $CaWO_4$ FOR EXCITATION BY X-RAYS

Added ions:	0.001 mol %	0 01 mol %	0 1 mol %	1 mol %
Cr	83	50	11.4	0
Fe	98	90	50	15
Mn	—	84.5	38.7	20.2
Cu	—	—	—	56.-

is strong. (Table XIX, Fig. 38). The correctness of our theory can be proved conclusively by studying the effects of a contamination, the extra absorption of which varies considerably over the range covered by the emission band: in this case not only the intensity, but also the spectral distribution of the emission must be changed. This condition is fulfilled by chromium, the absorption of which cuts off between 4000 and 5000 Å (see Fig. 38). Fig. 40 shows both intensity and spectral distribution of $CaWO_4$–Cr for various chromium contents, clearly revealing the anticipated variation in the spectral distribution of the emission.

Herewith our theory seems to be sufficiently proved. *The diminishing of the intensity of luminescence in calcium tungstate and magnesium tungstate — and probably also in other tungstates and in molybdates — effected by ions incorporated in the lattice*

is due to an ineffective[1] *additional absorption caused by these ions.*

The arguments in favour of the assumption that only par-
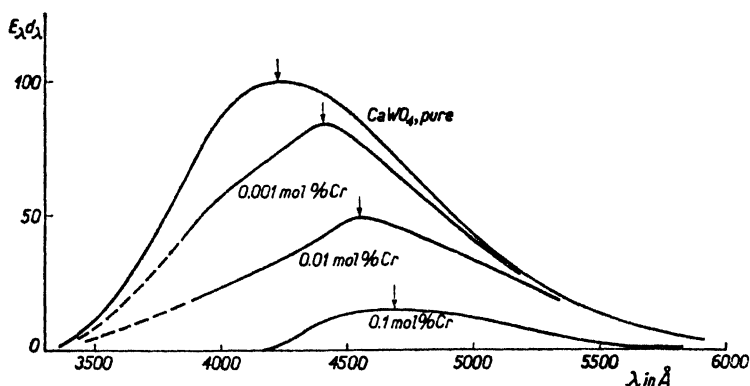
Fig. 40. Spectral distribution and intensity of the emission of $CaWO_4$ contaminated by various amounts of chromium for excitation by X-rays.

ticular tungstate or molybdate groups should be able to act as a centre of luminescence thus having been refuted, we are inclined to believe that — just as must be assumed for the absorption — all groups in the lattice are aequivalent with respect to luminescence: *any tungstate or molybdate group is able to give rise to emission.*

8. $CaWO_4$–Sm AND $CaWO_4$–Pb–Sm

It is known in the literature that rare earths embedded in calcium tungstate give rise to an emission characteristic of the ion concerned. For samarium, reports are to be found

[1] In some cases the additional absorption is not ineffective: $CaWO_4$–$PbWO_4$ (Section 5), $CaWO_4$–$CaMoO_4$ (Section 6), $CaWO_4$–*Sm* or other rare earths (Section 8). Then the intensity of the tungstate emission is diminished in the same way, but a new emission occurs instead. It depends on the efficiency of this new luminescence whether the total efficiency is diminished or even increased.

by URBAIN [1], DE ROHDEN [2], and SERVIGNE [3]. According to the latter author, at a sufficiently low temperature the orange samarium emission and the blue tungstate emission are emitted simultaneously. At a higher temperature the blue band disappears, whereas the samarium emission is reported to remain unchanged [3, 4, 5]. We have repeated these experiments.

The incorporation of samarium in $CaWO_4$ affects the absorption spectrum in two ways.' In the first place some comparatively faint, narrow absorption bands occur at 3650 and 4050 Å, characteristic of the trivalent samarium ion. In the second place the tungstate absorption band is slightly extended to the long wave-length side ($\sim$ 50 Å). This effect is probably due to perturbed tungstate groups in the neighbourhood of the samarium ions, just as was found with lead (Section 5).

Excitation in the characteristic samarium absorption bands leads to emission of the narrow samarium bands exclusively; the efficiency is nearly independent of temperature up to 300° C at least. Irradiation in the broad absorption band gives rise to the tungstate emission and the samarium emission simultaneously, in proportions dependent on the temperature. At —180°, excitation by radiation of a wave-length $\lambda < 2550$ Å, falling into the region corresponding to the absorption of pure $CaWO_4$, predominantly produces the blue band with only a comparatively faint orange luminescence; between 2600 and 2670 Å the orange emission predominates, whereas in the intermediate region the intensities for both emissions are of the same order. At higher temperatures the blue band decreases in all regions, eventually disappearing entirely. We have followed the process quantitatively for excitation by λ 2537 Å [6]. Fig. 41 shows the quantum efficiency of the separate emissions

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[1] G. URBAIN, *Ann. Chim.*, (8), **18** (1909) 293.
[2] A. DE ROHDEN, *Ann. Chim.*, (9), **3** (1915) 355.
[3] M. SERVIGNE, *C.R.*, Paris, **200** (1935) 2015; **203** (1936) 1247; **207** (1938) 905.
[4] J. T. RANDALL, *Trans. Far. Soc.*, **35** (1939) 12.
[5] W. DE GROOT, *Physica*, **7** (1940) 432.
[6] The measurements have been carried out by Mr TH. P. J. BOTDEN of this laboratory.

as a function of the temperature. We have assumed an effective wave-length of 4200 Å for the blue band, and of 6200 Å for the orange band. The blue band is nearly constant from —180°
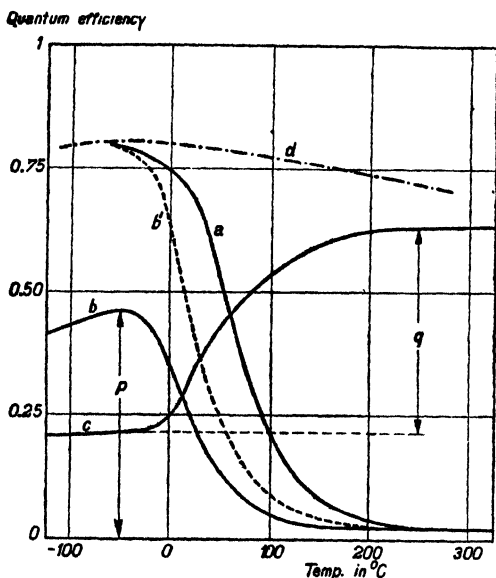
Fig. 41. Temperature dependence of the quantum efficiency of the luminescence of $CaWO_4$ and $CaWO_4$–Sm.

a. blue emission of pure $CaWO_4$ excited by λ 2537 Å.

b. blue emission of $CaWO_4$ – 1 mol % *Sm* excited by λ 2537 Å.

b'. idem, maximum arbitrarily fixed at the same level as the maximum for *a*.

c. orange *Sm* emission of $CaWO_4$ – 1 mol % *Sm*, excited by λ 2537 Å.

d. orange *Sm* emission of $CaWO_4$ – 1 mol % *Sm*, excited by λ 3650 Å (arbitrary units).

up to —40° C and then begins to decrease, at first slowly, then rapidly until it is totally quenched at 200° C. The decrease occurs in a temperature range which is about 20° C lower than that observed with pure $CaWO_4$. The samarium emission increases in the temperature range in which the blue

band decreases [1], remains constant at higher temperatures ($T > 200°$ C) and will probably be quenched at some temperature above 300° C. This point, however, was never reached in our experiments.

In addition Fig. 41 shows the variation of the efficiency [2] of the samarium luminescence upon excitation by λ 3650 Å into one of the characteristic samarium bands. The orange emission is nearly constant, at least does not show the discontinuity between —40 and +200° C. Hence the increase of intensity on excitation by λ 2537 Å cannot be due to some change in the emission process of the samarium ion. We have to assume instead that energy which was used for the blue emission at low temperatures, at higher temperatures arrives in some way at the samarium centre. A priori this could occur in two ways: either by a change in the absorption conditions, or by a transfer of energy, primarily absorbed in the tungstate groups to the samarium ions. In the first case we would have to assume separate absorptions for normal WO_4 groups surrounded by calcium ions and for perturbed groups near samarium ions. According to our absorption measurements, the absorption band of pure calcium tungstate, i.e., of "normal" tungstate groups, has a long wave-length limit near 2500 Å, while the absorption of tungstate groups near samarium ions must extend about 50 Å towards longer wave-lengths. On increasing the temperature both bands are extended to longer wave-lengths. For λ 2537, situated so near to the edge of the absorption of the unperturbed tungstate groups, we must expect that this absorption increases proportionately more

[1] This increase of the samarium emission is also revealed by Fig. 9, Plate IV of a publication by J. T. RANDALL, *Trans. Far. Soc.*, **35** (1939) 12.

[2] The quantum efficiency was found to be 2%. This value has no theoretic significance: the absorption of $CaWO_4$-Sm was identical with that of pure $CaWO_4$ within the margin of error, which indicates that the active samarium absorption is small compared with the extension of the tungstate absorption. If it would be possible to measure the exciting energy actually absorbed in the samarium ions, we would probably find a high quantum efficiency. Yet the temperature dependence as measured by us will not be markedly different from the correct one.

than the other one. Accordingly if changes of the absorption were responsible for the effect under discussion, the blue band ought to increase with increasing temperature at the cost of the orange band; just the opposite of what is actually observed. Moreover the effect does not occur exclusively on excitation in the neighbourhood of the edge of the tungstate absorption, but it occurs also on excitation with smaller wave-lengths in a region, situated less critically with regard to the absorption edge. Therefore we have to assume that transfer of energy takes place. An indication to the mechanism of this transfer of energy is provided by the near correspondence of the quenching range for the blue emission in $CaWO_4$–Sm with that in pure $CaWO_4$. Hence the energy absorbed in the tungstate absorption, which gives rise to the blue tungstate emission at low temperatures, is transferred to the samarium ions at temperatures at which the blue emission is quenched.

On excitation by λ 2537 Å the energy absorbed in the tungstate absorption band is probably distributed at random over all the tungstate groups in the irradiated part of the lattice, independent of whether they have samarium ions at neighbouring positions or not. Therefore the efficiency of the transfer may indicate whether it only occurs between tungstate groups and samarium ions at neighbouring positions, or whether the energy of all tungstate groups is transferred to the samarium ions, thus involving a transport of energy over several cells.

In the first case an upper limit to the transfer efficiency is determined by the fraction of tungstate groups which happen to have samarium ions at neighbouring positions. Since in $CaWO_4$ each tungstate group is surrounded by eight directly neighbouring metallic ions, the chance to find at least one samarium ion next to a certain tungstate group is eight times the samarium concentration and hence amounts to 8% for a product containing 1 mol % *Sm* as investigated by us. Accordingly the transfer efficiency cannot exceed 8% if this possibility is realized. On the other hand the efficiency may be as high as 100% when the energy transfer occurs over larger distances.

Such a high efficiency of transfer was actually observed: it was found to be 94% (*q*/*p*, Fig. 41). Hence we have to assume that at a temperature at which the tungstate emission is quenched, the energy absorbed in a tungstate group is transferred to a samarium ion, irrespective of whether the tungstate group happens to occupy a position next to it or not.

In $CaWO_4$ containing lead in addition to samarium, no complications occur in principle. The absorption spectrum consists of the characteristic narrow samarium bands and the tungstate absorption extending to ~ 3100 Å just as was observed with $CaWO_4$–$PbWO_4$. Irradiation into the samarium bands gives rise to the samarium emission; irradiation into the absorption region of $CaWO_4$ with $\lambda < 2550$ Å gives rise to the simultaneous emission of the orange samarium luminescence and the blue tungstate emission band III (cf. Section 5). The ratio between the orange emission and the tungstate emission is a function of the temperature, exactly as was described above for $CaWO_4$–*Sm*. The blue emission being totally quenched at 200° C, above this temperature the samarium emission occurs spectrally pure.

Excitation in the extension of the tungstate absorption between 2500 and 3100 Å, caused by lead, produces the samarium emission together with the tungstate emission II (cf. Section 5). The latter band is more persistent than the tungstate band III and is only totally quenched above 300° C. Hence, for excitation in this spectral region, at 200° C the emission still contains both the blue and the orange bands, and only above 300° C does it consist exclusively of the samarium bands [1]. It would be of interest to study the behaviour of the samarium emission as a function of the temperature with other systems where this emission is known to occur ($CaMoO_4$, $MgWO_4$, $CdWO_4$, $ZnWO_4$), and also with systems where it has not been found so far, but may occur below room temperature [2].

[1] Probably observations by W. DE GROOT, *Physica*, **7** (1940) 432 have not been carried out with $CaWO_4$–*Sm* — as stated — but with $CaWO_4$–*Pb*–*Sm* (cf. also our note on page 133 regarding a similar mistake.

[2] ''. P. JOHNSON–W. L. DAVIS, *J. Opt. Soc. Am.*, **29** (1939) 288.

Addendum

During the preparation of the manuscript the behaviour of the samarium fluorescence in some more systems has been studied (tungstates, molybdates, pure substances and mixed crystalls)[1]. Energy transfer was found to occur in several of these systems, though not in all. The most important results can be summarized in the following points:

1. The incorporation of samarium causes a lowering of the quenching range by 20–50° C, independent of whether energy transfer occurs or not.
2. If energy transfer occurs, the range in which the samarium fluorescence increases does not always coincide with the range in which the fluorescence of the tungstate or the molybdate decreases, but is sometimes situated at a considerably higher temperature, the total fluorescence showing a minimum in between.
3. The efficiency of the transfer varied from case to case. In one system, in which the tungstate fluorescence was rather faint, it was higher than 100%.

[1] TH. P. J. BOTDEN–F. A. KRÖGER, to be published in *Philips Res. Rep.*

IV. URANIUM AS AN ACTIVATOR

1. EMISSION, ABSORPTION AND EXCITATION

Luminescence connected with uranium is known both for uranium compounds and for systems activated by uranium, either in the crystalline or in the glassy states (cf. Table III, List 28). The emissions occurring are of two different types. The bands of the first type cover a broad wave-length range between 4600 and 6000 Å and show a fine structure which clearly indicates that they are built up of a number of equidistant sub-bands. The bands of the second type, situated in the red, are narrower and show only a vague fine structure (see Fig. 42).

The first, most frequently occurring bands are found with uranyl salts, uranyl glass ("canary glass") and most of the activated inorganic substances described by NICHOLS and SLATTERY [1]. They are closely related to a characteristic absorption occurring with these systems and are usually attributed to electronic transitions within uranyl-like configurations. The second bands, occurring far more rarely, were observed by JENKINS c.s. in $CaWO_4$ [2] and $CdWO_4$ [3] activated by 0.1–5% uranium, by ROBERTS with $SrWO_4$ [4], and by us with some other tungstates.

In our experiments, the tungstates activated by uranium were prepared by the method described previously for the pure tungstates (Chapter III, Section 2). The heating took place in an oxidizing atmosphere.

In Table XX we give a survey of the systems investigated together with the colour of the products and the roughly estimated intensity of the luminescence upon excitation by

[1] For references, cf. Table III, List 28.
[2] H. G. JENKINS–PINNER–MCKEAG, D.R.P. 711.437.
[3] H. G. JENKINS–PINNER–RYDE, B.P.S. 528.873.
[4] W. A. ROBERTS, U.S.A. Pat. 2.312.268.

TABLE XX
TUNGSTATES CONTAINING 1°/₀₀ OF WEIGHT U

Substance	colour	luminescence (excitation by λ 3650 Å) 25° C	luminescence (excitation by λ 3650 Å) —180° C	emission centre
$BaWO_4$	orange-yellow	*f.* yellow	*f.* yellow	?
$CaWO_4$	yellowish	*m.* green	*m.* green + *m.* red	uranyl + uranate
Ca_3WO_6	yellowish	*m.* green	?	uranyl
$CdWO_4$	brownish	*m.* red	*s.* red	uranate
Li_2WO_4	greyish	*m.* green	*m.* green	uranyl
$Li_2W_2O_7$	greenish	—	*f.f.* green	uranyl
$MgWO_4$	pink	*f.* orange	*s.* orange	uranate
Na_2WO_4	grey	—	—	—
$Na_2W_2O_7$	yellowish	*f.f.* green	*m.* orange + green	uranyl + uranate
$PbWO_4$	brownish pink	—	—	—
$SrWO_4$	*f.* pink	*f.* red	*f.* red	uranate
Sr_2WO_5	*f.* yellow	*s.* yellow green	*s.* yellow green	uranyl
Sr_3WO_6	?	—	—	—
$ZnWO_4$	brownish pink	*m.* orange-red	*s.* orange-red	uranate

s = strong *m* = medium *f* = faint *f.f.* = very faint.
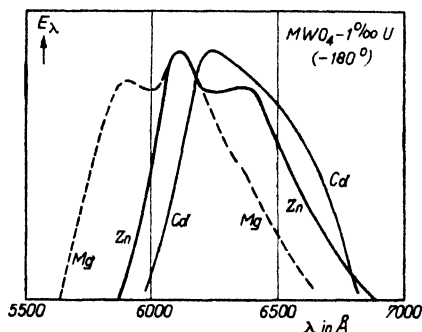
Fig. 42. Spectral distribution of the uranium emission at —180° C for excitation by λ 3650 Å.
a. $CdWO_4$ - 1°/₀₀ *U*
b. $MgWO_4$ - 1°/₀₀ *U*
c. $ZnWO_4$ - 1°/₀₀ *U*

λ 3650 Å, both at room temperature and at —180° C. As the emission of the tungstates themselves is not excited by this radiation, and the unactivated tungstates are all colourless, all the observed effects must be due to the uranium. In Fig. 42 we give the spectral distribution for some of the red emission bands; the bands seem to be built up of at least two sub-bands. For other systems we have only made a provisional photographic study. When temperature-quenching is eliminated as far as possible, i.e. at —180° C, most of the products show the long wave-length emission.

The emission bands of this type may be due either to uranium of a valency different from that found in the uranyl-radical, or to uranium of this valency but differently surrounded. For glasses the various possibilities of the state in which uranium may be incorporated have been studied extensively by FUWA [1], WEYL, c.s. [2], WEINBERG [3] and COLBERT and KREIDL [4]. Tetravalent uranium occurs under reducing conditions, hexavalent uranium under oxidizing circumstances. In basic glasses, i.e., glasses containing basic oxides in excess, the hexavalent uranium ions are present as uranyl groups; in acid glasses they are predominantly present as uranate groups. The uranyl glasses show the luminescence already mentioned, the uranate glasses are non-luminescent. Marked differences in the absorption also occur.

Since our products were prepared under oxidizing conditions, tetravalent ions are not to be expected; so we probably have to attribute our red emission bands to uranate groups.

The absorption phenomena support this view. In agreement with the effects reported for glasses, there is a marked difference in absorption between the products showing the uranyl emission, which are coloured slightly yellowish, and the red lumines-

[1] K. FUWA, *Mazda Kenkyu-Jiho*, **3**, nr 1.

[2] W. WEYL-E. THÜMEN, *Sprechsaal*, **67** (1934) 95.
C. KÜHL-H. RUDOW-W. WEYL, *ibid.*, **71** (1938) 91, 104, 117.
W. WEYL, *J. Soc. Glass Techn.*, **28** (1944) 240; *Ind. Eng. Chem.*, **34** (1942) 1035.

[3] T. I. WEINBERG, *C. rend. acad. sci. U.R.S.S.*, **46** (1945) 318.

[4] W. COLBERT-N. J. KREIDL, *J. Opt. Soc., Am.*, **35** (1945) 731.

cent products which are pink. The uranyl absorption shows a fine structure similar to that of the emission and cuts off somewhere near 5000 Å; the uranate absorption does not show much of a structure and extends over the visible up to the red. In both cases the emission is situated at the long wave-length end next to the absorption, slightly overlapping it near the edge.

The absence of the uranate emission in glass which might be brought up as an argument against our supposition need not disturb us. We recently found that it is due to temperature quenching, an emission of this kind actually occurring at low temperatures [1].

Once the distinction between uranate emission and uranyl emission has been made and accepted, we must not take these terms too literally. An uranyl-like emission is observed with substances like UO_3 and $Na_2U_2O_7$. (—180° C) where the assumption of UO_2^{2+} groups seems rather artificial, while in other cases in which no oxygen is present, such as in NaF and KF (SLATTERY, *loc. cit.*), the assumption of these ions is obviously absurd. The essential factor determining the character of the emission is probably the environment of the hexavalent uranium ion. For the uranyl-like emissions this environment must resemble that of the configuration existing in the uranyl salts. In the uranates a different situation exists.

Keeping these restrictions in mind, we give in the last column of Table XX the probable attribution of the emissions observed with the tungstates activated by uranium. In most cases either the uranyl emission or the uranate emission occurs alone. With $CaWO_4$ they are emitted simultaneously [2].

The excitation phenomena are explained by the assumption of two broad absorption bands. The first band is the tungstate absorption, as existing in the unactivated tungstates also,

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[1] F. A. KRÖGER–J. M. STEVELS–TH. P. J. BOTDEN, *Philips Res. Rep.*, **3** (1948) 46.

[2] JENKINS (*loc. cit.*) reports a yellow emission for this system, whereas the visual impression of the luminescence of our sample was nearly green. This discrepancy may be caused by a difference in the intensity ratio between the two bands, due to influences so far unknown.

with a long wave-length limit near 2600 Å. The second band is the absorption correlated with the uranium, either uranyl or uranate absorption. As mentioned above, it covers part of the visible, but probably also extends into the ultra violet, coinciding with the much stronger tungstate absorption. Irradiation in that part of the uranium absorption not covered by the tungstate absorption gives rise to the uranyl or the uranate emission. Excitation into the short-wave region where the two absorption bands are superposed, causes luminescence in the tungstate and uranium emissions simultaneously. The tungstate emission predominates since in this region the tungstate absorption is much stronger than the uranium absorption.

2. TEMPERATURE DEPENDENCE OF LUMINESCENCE

The temperature dependence of the uranium emissions, indicated for our products in Table XX, was measured
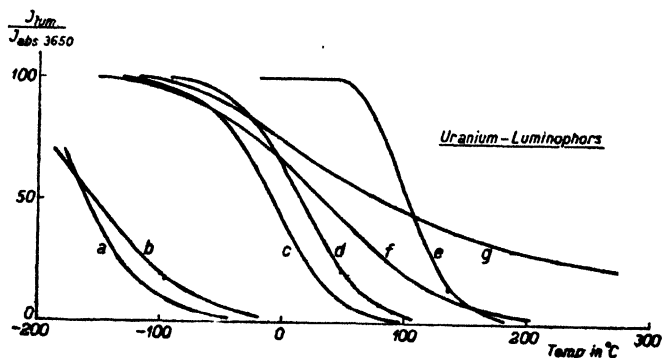
Fig. 43. Temperature dependence of the luminescence of some uranium luminophors for excitation by λ 3650 A°:

a. $MgWO_4$ – 0.1 mol % U } uranate emission
b. $ZnWO_4$ – 1 mol % U
c. $CdWO_4$ – 0.01 to 1 mol % U

d. Sr_2WO_5 – 0.1 mol % U } uranyl emission
e. $(NH_3)_3UO_2F_5$
f. silicate glass – 2 % U^3O_8 (identical results for exc. by 2537 A°)
g. uranyl glass (GIBBS)

in certain cases (Fig. 43). In all cases the efficiency increases towards low temperatures. Some products like $ZnWO_4$–U and $MgWO_4$–U, hardly luminescent at room temperature, become luminescent at —180°. $CdWO_4$–U and Sr_2WO_5–U, the single tungstates that show a considerable uranium emission at room temperature, yet reach their maximum intensity only
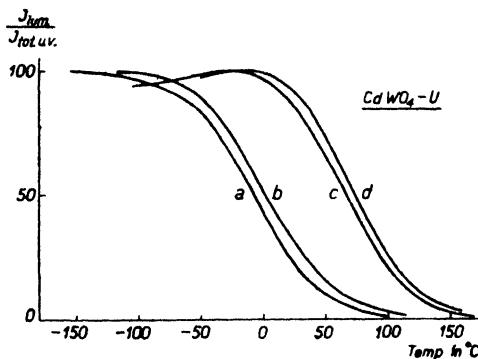
Fig. 44. Temperature dependence of the luminescence of $CdWO_4$ and $CdWO_4$–U

a. red emission of $CdWO_4$ - 1 mol % U excited by λ 3650 Å.
b. red emission of $CdWO_4$ - 1 mol % U excited by λ 2537 Å.
c. blue emission of $CdWO_4$ - 1 mol % U excited by λ 2537 Å.
d. blue emission of pure $CdWO_4$ excited by λ 2537 Å.

at —100° C. We also give the temperature dependence of uranyl glass according to OVERBEEK [1] and GIBBS [2]. The extremely flat shape of the latter curve must probably be correlated with the complexity of the emission spectrum, the glass investigated by GIBBS [2] showing a green and a red emission in proportions which changed with the temperature. A similar continuous decrease of the emission was also observed by RODRIGUEZ c.s. [3]. For $CdWO_4$–U we have compared the temperature dependence of the luminescence for various

[1] J. TH. G. OVERBEEK, private communication.
[2] R. C. GIBBS, *Phys. Rev.*, **28** (1901) 360; **30** (1910) 377.
[3] A. R. RODRIGUEZ–C. W. PARMELEE–A. E. BADGER, *J. Am. Cer. Soc.*, **26** (1943) 137.

methods of excitation in order to see whether similar effects to those found with $CaWO_4$–Sm occurred. As is shown by Fig. 44 the temperature dependence of the uranate emission is independent of the method of excitation, being practically identical when excited singly in the long-wave region (λ 3650 Å) or together with the tungstate emission in the short-wave region ($\lambda < 2600$ Å). The temperature quenching of the tungstate emission of $CdWO_4$–U excited with $\lambda < 2600$ Å occurs in nearly the same temperature range as with the unactivated tungstate. Hence, unlike $CaWO_4$–Sm, no interaction seems to occur between the mechanisms of the blue and the red band.

V. TITANIUM AS AN ACTIVATOR

1. GENERAL OBSERVATIONS

A blue cathodo-luminescence due to titanium acting as an activator has been found independently in Zn_2SiO_4 [1] and $MgSiO_3$ [2].

We have been able to prove that the effects of this ion are not in the least haphazard, and that titanium is universally able to cause luminescence. For this purpose we have prepared a large number of compounds, pure and with addition of titanium, under both oxidizing and reducing conditions.

For the preparation we started with solutions of compounds of the components, mostly nitrates or acetates. A solution of titanium was obtained as previously described (Chapter II, Section 2.2.1) After mixing the solutions in suitable proportions, concentrated ammonia is added to precipitate the ions completely in the form of hydroxides; the supernatant liquid is evaporated by heating at about 95° C in a waterbath or on an electric stove, and the dry hydroxides obtained are decomposed into oxides by heating at a moderate temperature ($\sim$ 500° C). The thorough mixture of oxides thus obtained is finally fired for 2 hours in an oxidizing (oxygen, air) or reducing (H_2, H_2+N_2) atmosphere.

Emissions are only observed with the oxidized products. The activated samples prepared under reducing conditions are coloured blue due to reduction of the incorporated titanium, and do not show any luminescence. Hence luminescence effects correlated with titanium must be attributed to titanium in its highest valency state, i.e., to tetravalent Ti^{4+}.

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[1] FRENCH. PAT. SPEC. 869.448; results by LEVERENZ and SEITZ (Phys. Rev., **53** (1938) 919; *J. Appl. Phys.*, **10** (1939) 479, regarding the influence of titanium upon the emission properties of zinc-beryllium sillicates activated by manganese, point in the same direction but were interpreted wrongly: the effect was assumed to be due to a modification of the matrix lattice rather than to a real activation.

[2] FRENCH. PAT. SPEC. 896.650.

TABLE XXI

LUMINESCENCE EXCITED BY CATHODE RAYS

Substance	unactivated		activated by 1 mol % *Ti*		Remarks
	25°	—180°	25°	—180°	
Aluminates					
$CaAl_2O_4$	—	—	—	—	
$La_2Al_2O_6$	—	—	—	—	
$MgAl_2O_4$	—	—	—	—	
$SrAl_2O_4$	—	—	—	—	
$ZnAl_2O_4$	*f.* green	*f.* green	*f.* blue	?	*Mn*
Borates					
CaB_2O_4	*f.f.* blue	*f.f.* blue	*f.f.* blue	*f.f.* blue	unknown act.?
$Ca_2B_2O_5$	*f.f.* blue	*f.f.* blue	*f.f.* blue	*f.f.* blue	,,
$Cd_2B_2O_5$	*f.* red	*f.* red + *f.* blue	*f.* red	*f.* red + *f.* blue	red ≡ *Mn*
ZnB_2O_4	—	—	—	—	
$Zn_3B_2O_6$	*f.* orange	?	*f.* orange	?	*Mn*
Boro-phosphates					
$Ca(BP)O_3$	*f.f.* blue	*f.f.* blue	*f.f.* blue	*f.f.* blue	unknown act.?
$Mg(BP)O_3$	*f.* orange	*f.* orange	*f.* orange	*f.* orange	*Mn*
$Zn(BP)O_3$	—	—	—	—	
Oxides					
Al_2O_3	*f.* red	*f.* red	*f.* red	*f.* red	*Mn*
CaO	*f.* red	*f.* red	*f.* red	*f.* red	*Mn*
MgO	—	—	—	—	
SiO_2	—	—	*f.* white-blue	*f.* white-blue	
ThO_2	—	—	*f.* white	?	
ZrO_2	—	—	*s.* green	*s.* green	
Phosphates					
$AlPO_4$	—	—	—	—	
$Ca_2P_2O_7$	—	—	—	—	
$Ca_3(PO_4)_2$	—	—	—	—	
$Cd_2P_2O_7$	*f.* red	*f.* red	*f.* red	*f.* red	*Mn*
$Cd_3(PO_4)_2$	*f.f.* blue	*f.f.* blue	*f.* blue	*f.f.* blue	unknown act.?
$Mg_2P_2O_7$	*f.* red	?	*f.* red	?	*Mn*
$Mg_3(PO_4)_2$	?	?	*f.* red	?	*Mn*
$Zn_2P_2O_7$	*f.* orange	*f.* orange	*f.* orange	*f.* orange	*Mn*
$Zn_3(PO_4)_2$	*f.* green	*f.* green	*f.* green	*f.* green	*Mn*

TABLE XXI
(continued)

Substance	unactivated		activated by 1 mol % *Ti*		Remarks
	25°	—180°	25°	—180°	
Silicates					
Ba_2SiO_4	—	—	*f.f.* white-blue	*f.f.* white-blue	
$BaSiO_3$	—	—	*s.* white-blue	*s.* white-blue	
Ca_2SiO_4	—	—	*f.* blue	*f.* blue	
$CaSiO_3$	—	—	*s.* blue	*s.* blue	
Cd_2SiO_4	—	—	—	*f.* blue	
$CdSiO_3$	*f.* red	*f.* red	*m.* white-blue	*m.* white-blue	red ≡ *Mn*
$La_2Si_2O_7$	*f.* red	*f.* red	*f.* red + *f.* blue	*f.* red + *f.* blue	red ≡ *Sm*
Li_2SiO_3	—	—	*f.* blue	*f.* green	
$Li_2Si_2O_5$	—	—	*s.* white-blue	*s.* white-blue	
Li_4SiO_4	—	—	*m.* blue	*f.* blue	
Li_2CaSiO_4	—	—	*f.* blue	?	
Mg_2SiO_4	*m.* red	*m.* red	*f.* blue + red	*f.* blue + red	red ≡ *Mn*
$MgSiO_3$	—	—	*s.* blue	*s.* blue	
$(MgCa)SiO_3$	—	—	*s.* white-blue	*s.* white-blue	
$Na_2Ca_2Si_3O_9$	—	—	*m.* blue	?	
Na_2SiO_3	—	—	*m.* blue	?	
$Na_2Si_2O_5$	—	—	*s.* white-blue	*s.* white-blue	
Na_4SiO_4	—	—	*f.* blue	*m.* green	
$PbSiO_3$	—	—	—	—	
Pb_2SiO_4	—	*m.* yellow	—	*m.* yellow	*Pb*?
Sr_2SiO_4	—	—	*f.* blue	*f.f.* blue	
$SrSiO_3$	—	—	*m.* blue	*m.* blue	
Zn_2SiO_4	—	—	*s.* blue	*s.* blue	
$(ZnBe)_2SiO_4$	—	—	*s.* blue	*s.* blue	
Stannates					
Ba_2SnO_4	—	*m.* yellow green	*m.* blue	*m.* blue + yell. green	yell.green ≡ *Sn*
$BaSnO_3$	—	orange	—	orange	*Sn*
Ca_2SnO_4	—	—	*s.* blue	*s.* blue	
$CaSnO_3$	—	—	*f.* blue	*f.* blue	
$CdSnO_3$	—	—	*m.* yellow	*m.* yellow	

TABLE XXI
(continued)

Substance	unactivated		activated by 1 mol % *Ti*		Remarks
	25°	—180°	25°	—180°	
Mg_2SnO_4	*m.* blue-green	*m.* blue-green	*s.* white-blue	*s.* white-blue	blue-green ≡*Sn*
$MgSnO_3$	*m.* green	*m.* green	*f.* green	*f.* green	*Sn*
Sr_2SnO_4	—	—	*s.* blue	*s.* blue	
$SrSnO_3$	—	—	—	*m.* blue	
Zn_2SnO_4	*f.* orange	*f.* orange	*f.* orange	*f.* orange	*Sn*
$ZnSnO_3$	*f.* orange	*f.* orange	*f.* orange	*f.* orange	*Sn*
Zirconium-compounds					
$BaZrO_3$	—	—	—	deep blue	
$CaZrO_3$	—	—	deep blue	deep blue	
Na_2ZrO_3	—	—	green	green	
Na_2ZrSiO_5	—	—	green	green	
$SrZrO_3$	—	—	—	deep blue	
$ZrSiO_4$	—	—	white	white	
$Zr_3P_2O_7$	—	—	*f.* blue	?	

s = strong *m* = medium *f* = faint *f.f.* = very faint.

In Table XXI we give a survey of the systems prepared under oxidizing conditions, together with the luminescence effects at 25° C and at —180° C. Comparison of the luminescence of corresponding activated and unactivated samples reveals the influence of titanium; a blue emission which is observed with the activated products, but not found in the unactivated products, must be due to the activator. Titanium thus proves to be effective in compounds of silicon [1], tin, zirconium, and thorium, but not in compounds of aluminium, phosphorus or boron when one of the elements mentioned above is not present. Obviously the activator must be built in isomorphously, which is only possible in the compounds

[1] Blue emissions observed with unactivated silicates of *Cd*, *Ca*, *Sr* and *Ba* may well have been caused by traces of titanium. (H. W. Leverenz, *R.C.A. Review*, **5** (1940) 131).

of the tetravalent ions mentioned, the ionic radii of which do not differ too much from those of the tetravalent titanium ion. The formation of mixed crystals was actually proved for the systems $MgSiO_3$–$MgTiO_3$, and $CaSiO_3$–$CaTiO_3$ by means of *X*-ray diffraction photographs. In the first system two regions of solid solutions occur. One extends from 0–27 mol % $MgTiO_3$ (1350° C) and shows the klino-enstatite structure [1]. The second occurs between 42–65 mol % $MgTiO_3$. The solubility of $MgSiO_3$ in $MgTiO_3$ with its own structure is practically zero. In the same way a-$CaSiO_3$ proved to be capable of dissolving ~ 8 mol % $CaTiO_3$ at 1350° C, $CaTiO_3$ ~ 35 mol % $CaSiO_3$ [2].

The amounts of titanium present in the samples as listed in Table XXI correspond roughly to the optimum concentration with regard to luminescence. It is remarkable that these concentrations, being on the average 10 mol %, are considerably higher than is usual for activation. Luminescence also occurs with products containing far more titanium such as $MgSiO_3$–60 mol % $MgTiO_3$, while even some pure titanates show an emission (Mg_2TiO_4, $MgTiO_3$).

2. ABSORPTION

Most of the matrix substances of the systems under investigation show an absorption cutting off in the short-wave part of the ultra violet. For the silicates and silica the edges are situated at $\lambda < 2200$ Å in the region inaccessible to normal spectography. With the stannates the long wave-length limit of the absorption is between 2300 and 2600 Å; ZrO_2 shows an edge at 2370 Å. The products containing titanium all show an absorption extending to longer wave-lengths, the edges

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[1] Pure $MgSiO_3$ occurs either in the proto-enstatite or in the klino-enstatite modification. The latter structure is stabilized by titanium in the same way as was observed for *Li* and *Ca* by W. BÜSSEM and C. SCHUSTERIUS, *Wiss. Veröffentl. Siemens*, **17** (1938) 59.

[2] This result is in contradiction with observations by S. SMOLENSKY who found an uninterrupted series of mixed crystals at this temperature (*Z. anorg. Chem.*, **73** (1912) 294.

being situated between 2700 and 3600 Å in the same region in which the absorption edges of the pure titanates are found (cf. Fig. 45 and 46). Obviously we are concerned with an absorption of the characteristic type, correlated with titanium.
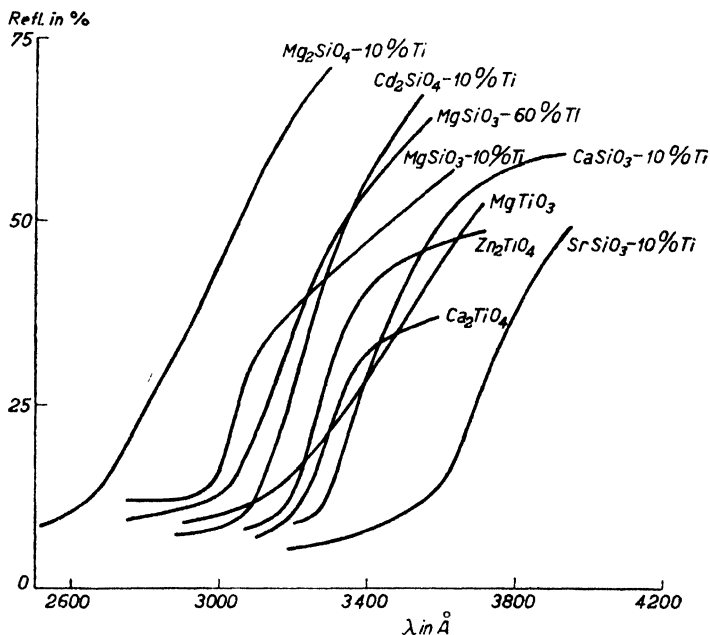
Fig. 45. Spectral distribution of the reflection of titanates and solid solutions of silicates with titanates at —180° C.

The tetravalent titanium ion alone is not to be expected to be responsible for these effects: it is completely stripped of its outer electrons and shows a rare-gas-like electronic configuration. Instead the absorption must be due to some configuration common to all the systems. Probably it is formed by titanium and adjacent oxygen atoms. The situation shows much resemblance to those of the tungstates, molybdates, uranates, stannates, and plumbates.
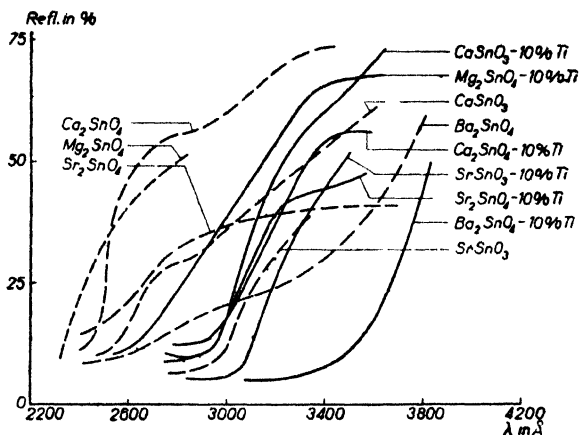
Fig. 46. Spectral distribution of the reflection of stannates and mixed crystals of stannates and titanates.
dotted curves: pure stannates
fully drawn curves: mixed crystals containing 10 mol % *Ti*.

3. EXCITATION

In Table XXII we give a survey of the excitation phenomena at —180° C, together with the position of the absorption edges of both activated and unactivated substances. The activated substances show luminescence upon irradiation into the absorption system of the matrix lattice or into the titanate absorption. Depending on the wave-length of the exciting radiation two different emissions occur. In a long-wave region, limited at the long-wave side by the titanate absorption edge, the luminescence varies between green and orange-yellow. In the adjoining region, extending deeply into the ultra violet, a blue emission is excited. The latter luminescence is identical with the emission produced by cathodic bombardment. The limit between the two excitation regions bears no relation whatsoever to the absorption edge of the matrix lattice. For instance, in $MgSiO_3$ it is situated at 2550 Å, whereas the absorption edge of unactivated $MgSiO_3$ must

be somewhere below 2200 Å; in Cd_2SiO_4 with an absorption edge near 2400 Å, it is situated at 2850 Å, etc. Hence the different excitations must both occur in the absorption system of the titanate. Just as was proposed for the very similar phenomena obtained with $PbWO_4$ (Chapter II, Section 3), we have to assume two different, partly overlapping absorption bands, each corresponding to one of the two observed emissions. Whether these two bands are due to different electronic transitions in the same titanate groups or to transitions in different titanate configurations remains an open question. We are personally inclined to believe that the first possibility is realized.

Although the correlation long wave-length emission ←→ long wave-length absorption and short wave-length emission ←→ short wave-length absorption is found to exist in each system we do not find a quantitative relation connecting the wave-length of the emission with the long wave-length limit of the corresponding absorption which holds for all titanium luminophors. Unlike the situation in the tungstates and the molybdates where the gap between absorption and emission
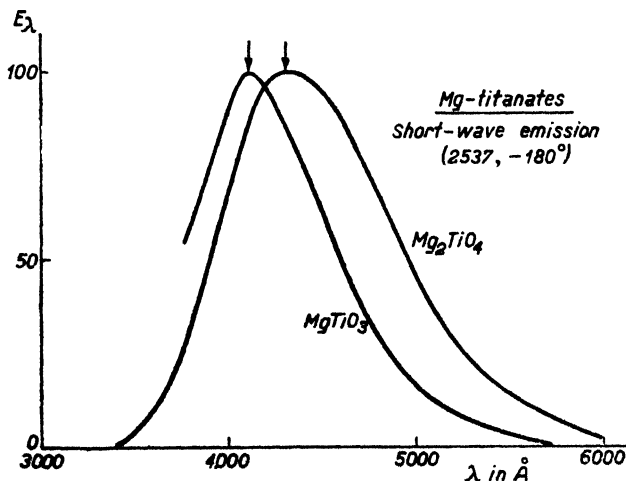
Fig. 47. Spectral distribution of the luminescence of magnesium titanates at —180° C.

TABLE XXII

LUMINESCENCE, EXCITATION AND ABSORPTION AT —180° C

No.	Substance	Activ. by mol % Ti	Long-wave excitation: Colour of lum.	Long-wave excitation: Excitation region	Short-wave excitation: Colour of lum.	Short-wave excitation: Excitation region	Abs. edge matrix lattice	Abs. edge activ. subst. (10 mol % Ti)	Remarks	No.
1	Ba_2SiO_4	10	yell. green	? —2450	blue	<2450				1
2	$BaSiO_3$	10	?	? —2700	white blue	<2700				2
3	$CaSiO_3$	10	yell. green	3350—2500	blue	<2550	<2200	~3350		3
4	Cd_2SiO_4	10	or. yellow	3200—2850	white	<2850	~2400	3140		4
5	$CdSiO_3$	10	yellow	3350—2600	blue	<2600	~2400			5
6	$Li_2Si_2O_5$	5			green	<2660			blue cath. lum.	6
7	Li_2SiO_3	1	yell. green	3650—2450	—	—				7
8	Mg_2SiO_4	10	or. yellow	3200—2660	blue	2660				8
9	$MgSiO_3$	10	green	3200—2550	blue	<2550	<2200	3000		9
10	$MgSiO_3$	60	green	3200—2800	blue	<2800		~2900 *	* 60% Ti	10
11	$Na_2Si_2O_5$	5	green	3000—2200	blue	<2450				11
12	Na_2SiO_3	10	yell. green	3200—2450	—	—				12
13	$SrSiO_3$	10	yell. green	3650—2450	blue	<2450	<2200	~3650		13
14	Zn_2SiO_4	1	yellow	3200—2450	blue	<2450	~2200	3300		14
15	$MgTiO_3$		green	3200—2700	blue	<2700	~3100			15
16	Mg_2TiO_4		green	3200—2800	blue	<2800	~2900			16
17	SiO_2	10	green	<~3500	green					17
18	ThO_2	1	?	<3200	?					18
19	ZrO_2	1	green	<3650	green		2370	3500		19
20	$BaZrO_3$	1								20
21	$CaZrO_3$	1	green	3200—2800	blue	<2900				21
22	$SrZrO_3$	1								22
23	ZrP_2O_7	1	green	<3300	green		<2300	~3000		23
24	$ZrSiO_4$	1	green	<3350	green		2350	3330		24
25	Ba_2SnO_4	1	orange	3150—3050	blue	<3050	2600	3600	<2800 somewhat greenish; Sn ?	25
26	Ca_2SnO_4	10		[illegible]	blue	<3200	2500	3200		26
27	$CaSnO_3$	10	yellow	3150—2900	blue	<3050	2600	3100		27
28	Mg_2SnO_4	10	or. yellow	3200—2780	blue	<2800	2300	2700		28
29	$MgSnO_3$	10	yellow	3300—2550	blue	<2600	3200	3200		29
30	Sr_2SnO_4	10	yell. green	3200—2900	blue	<3020		3030		30
31	$SrSnO_3$	10	yell. green	3350—3000	blue	<3050	2880	3100		31

is nearly constant, in this case the displacement of the emission with respect to the absorption is highly variable, probably depending on variations in the configuration of the titanium and the adjacent oxygen atoms.

4. EMISSION

The spectral distribution of the emission of magnesium titanates and of some activated silicates, stannates, and zirconates is shown in Fig. 47, 48 and 49. For the silicates

the short wave-length emission was excited by cathodic bombardment, for the stannates and zirconates it was excited
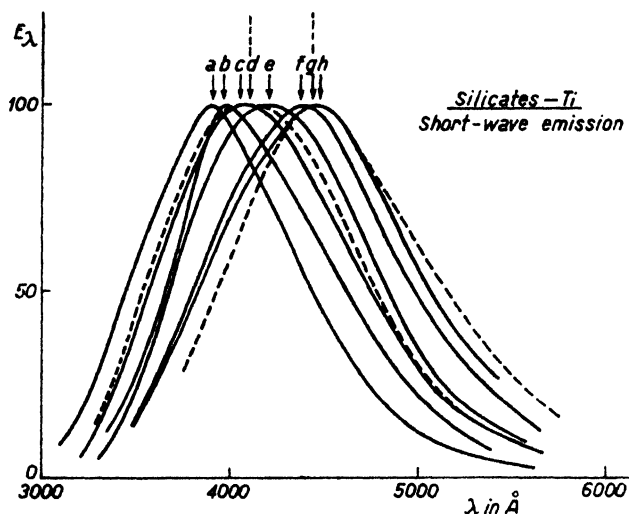
Fig. 48. Spectral distribution of the cathodo-luminescence of silicates, activated by titanium, at room temperature.

a. Zn_2SiO_4 — 1 mol % *Ti*
b. $SrSiO_3$ — 10 mol % *Ti*
c. $MgSiO_3$ — 10 mol % *Ti*
d. $Li_2Si_2O_5$ — 5 mol % *Ti*
e. $(Ca\text{–}Mg)SiO_3$ — 10 mol % *Ti*
f. $CaSiO_3$ — 10 mol % *Ti*
g. $CdSiO_3$ — 10 mol % *Ti*
h. $Na_2Si_2O_5$ — 1 mol % *Ti*

by λ 2537 Å. The long wave-length bands were excited by λ 3130 Å. Both kinds of emission bands vary slightly in their position on the wave-length scale, just as was observed for the absorption edges of the various systems.

5. TEMPERATURE DEPENDENCE OF LUMINESCENCE

The temperature dependence of the luminescence of the silicates, titanates, and stannates is given in Fig. 50 and 51.

The units are arbitrary, all maxima having been fixed at 100. Most of the curves refer to blue emissions; in some cases where
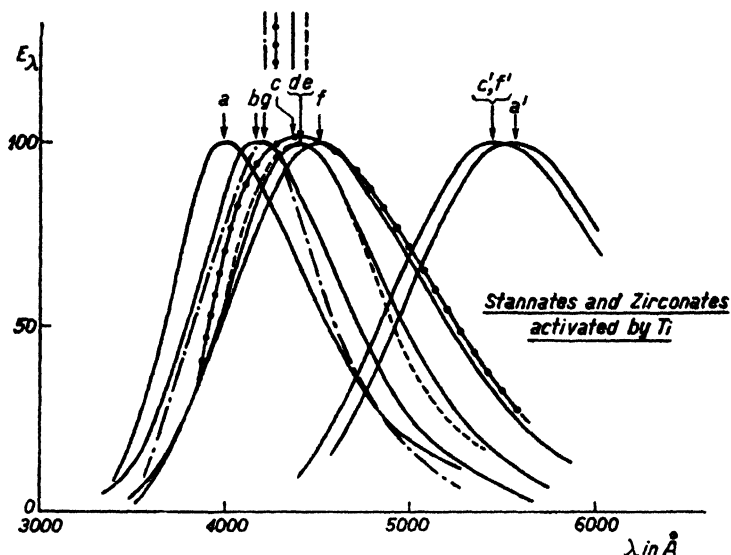
Fig. 49. Spectral distribution of the luminescence of stannates and zirconates, activated by titanium:

a. $CaSnO_3$ - 10 mol % *Ti* at —180° C, excited by λ 2537.
a'. idem, excited by λ 3130.
b. Sr_2SnO_4 - 1 mol % *Ti* at 25° C, excited by λ 2537.
c. $MgSnO_3$ - 10 mol % *Ti* at 25° C, excited by λ 2537.
c'. idem excited by λ 3130.
d. Ca_2SnO_4 - 1 mol % *Ti* at 25° C, excited by λ 2537.
e. $SrSnO_3$ - 1 mol % *Ti* at —180° C, excited by λ 2537.
f. Mg_2SnO_4 - 1 mol % *Ti* at 25° C, excited by λ 2537.
f'. idem, excited by λ 3130.
g. $CaZrO_3$ - 1 mol % *Ti* at —180° C, excited by λ 2537.

both green and blue emissions were measured the colour is indicated on the curve. The method of excitation is also marked.

The temperature quenching of the luminescence, determined by the decreasing part of the curves, is nearly conformal for all systems, but sets in at quite different temperatures. The most persistent emission was found with Li_4SiO_4–*Ti*,
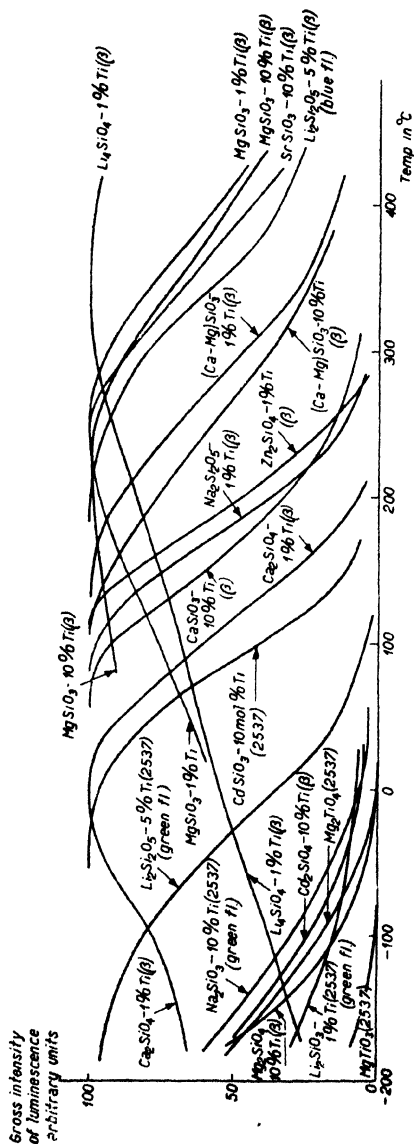
Fig. 50. Temperature dependence of the luminescence of silicates activated by titanium for excitation by cathode rays (β) and λ 2537 Å.

which showed no appreciable quenching even at 400° C. With some of the systems, viz., $MgSiO_3$, Li_4SiO_4 and probably other ones which were not accurately measured in the region con-
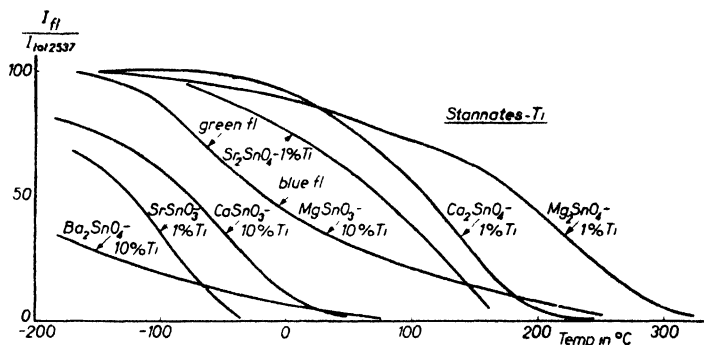
Fig. 51. Temperature dependence of the luminescence of stannates, activated by titanium.

cerned, the luminescence increases with the temperature up to the point where the temperature quenching sets in, neutralizing it at first and then over-compensating it. We are unable to offer an explanation. A second emission which might occur in the low temperature region would provide an explanation (cf. Chapter VI, Section 3.3) but could not be detected. Some of the quenching curves measured with the stannates show an aberrant shape due to the occurrence of a stannate emission besides the titanate emission. In Fig. 51 this is indicated by marking the colour of the luminescence corresponding to the various parts of the curves.

The metastannates of *Ca*, *Sr* and *Ba*, all crystallizing in the perovskite structure[1] and the orthostannates of these same elements which according to our own *X*-ray diffraction photographs are probably also isomorphous, present examples of the systematic change of the temperature quenching in a normal sequence (cf. Chapter VI, Section 3).

[1] *Struktur-Ber.*, **1** (1913—1928) **303**; **3** (1933—1935) **68**.

6. DECAY

The decay of luminescence after interruption of the excitation was measured by Mr J. VAN DER MARK of this laboratory for $MgSiO_3$–10 mol % $MgTiO_3$ upon excitation by β-rays. It proved to be purely exponential with a time constant $\tau \sim 2.6 \cdot 10^{-4}$ sec.

7. COMPLEX FLUORIDES ACTIVATED BY TITANIUM

As was made probable in the previous sections, the luminescence and absorption of the titanium luminophors must be attributed to electronic transitions in configurations formed by titanium and the atoms surrounding it. In the cases studied above, containing oxygen as the negatively charged constituent, the configuration must be Ti–O_x. If however, titanium was surrounded by a different kind of atoms, the complexes would be different too, and would show different optical properties. It has been possible to fulfil this condition with the complex fluorides of tin, silicon, and titanium.

K_2TiF_6, K_2SiF_6 and K_2SnF_6 were obtained as the less soluble part of the reaction product of molten KHF_2 with TiO_2, SiO_2 or SnO_2. Na_2SiF_6 was prepared in a similar way by means of $NaHF_2$; $CaSiF_6$, $SrSiF_6$, $BaSnF_6$, $SrSnF_6$ and $CaSnF_6$ were precipitated from the dilute solutions of the corresponding sodium or potassium compounds by addition of a solution of *Ba, Sr* or *Ca* nitrate. The activated products were obtained by substituting for part of the *Sn* or *Si* compounds the corresponding *Ti* compounds during the first stage of the preparation. The precipitated products were heated at 500° C in order to obtain better formed crystals of a larger size. Some NH_4F added kept the air out of the crucible and thus prevented oxidation.

Table XXIII shows the results. At low temperatures all activated products show an emission, varying from yellow to orange, which does not occur with the pure substances and hence must be due to titanium. These emissions are excited without exception in a region below $\lambda = 3100$ Å. A shortwave part of the absorption system, as was observed with the oxygen compounds, does not occur.

TABLE XXIII

Substance	Luminescence (excitation λ 2537 Å)				Excitation region (Å)
	unactivated		activated (10 mol % *Ti*)		
	25°	—180°	25°	—180°	
K_2TiF_6	—	*m.* orange yellow		idem	<3100
K_2SnF_6	—	—	*f.f.* yell.	*m.* yellow	<3100
K_2SiF_6	—	—	—	*m.* yellow	<3100
Na_2SiF_6	—	—	—	*f.* yellow	<3100
$PbSiF_6$	—	*f.* green blue	—	*f.f.* orange	2537
$BaSnF_6$	—	—	—	*s.* green-yellow	<3100
$CaSnF_6$	—	—	—	*m.* yellow	2537
$SrSnF_6$	—	—	—	*f.* yellow	2537
$CaSiF_6$	—	—	—	*f.f.* orange	2537

s = strong *m* = medium *f* = faint *f.f.* = very faint.

Thus although TiF_x shows an emission differing to some extent from that of the TiO_x configurations, yet the similarity is so great, that the central ion must play a preponderant part in the processes, in the same way as was concluded for the complexes of thallium, lead and tin (cf. Chapter I, Section 14).

VI. THE DEPENDENCE OF THE EFFICIENCY OF LUMINESCENCE ON THE TEMPERATURE

1. INTRODUCTION

In all substances, absorption of radiant energy, especially ultra violet radiation, *X*-rays or corpuscular rays, gives rise to excitation of electrons. As far as we know, this process is completely independent of temperature. The inverse process, however, the return of the excited electrons to the ground state accompanied by the emission of radiation, does not occur to the same extent at all temperatures. It is generally known that in substances showing luminescence at room temperature the luminescence is quenched at some higher temperature [1]; on the other hand, many substances which are not luminescent at room temperature show this phenomenon at low temperatures [2].

Obviously, the dependence of the intensity of the luminescence on the temperature is extremely interesting from a theoretical point of view. As a matter of fact, it constitutes one of the most fundamental problems in this field. Yet, although much attention has been paid to many aspects of the luminescence in solids, the influence of the temperature, though not having been totally neglected, has been only considered occasionally, and satisfactory experimental data are lacking. Accordingly many questions on this aspect are yet to be answered. What is the mechanism of the temperature quenching? In what way does it depend on the configuration of the centres in the luminophor, the crystal structure and the constituents of the matrix lattice and the concentration of the activators? Is it possible to reach a quantum efficiency of 100% by cooling in all cases, or are there other factors limiting the efficiency? If so, what are these factors? .... etc.

[1] P. LENARD–V. KLATT, *Ann. d. Phys.*, **15** (1904) 452.
[2] J. T. RANDALL, *Trans. Far. Soc.*, **35** (1939) 1.

On the other hand, the temperature dependence is also important from a practical point of view; particularly in testing luminophors to be used in engineering. A luminophor showing its optimum intensity only at low temperatures is obviously automatically discarded upon testing at room temperature even when we do not know anything about the temperature dependence. When the temperature quenching sets in near room temperature, however, the luminophor may be intense and seem useful upon testing at room temperature, but may be totally useless at the actual working temperature which is usually somewhat higher. In these cases a temperature dependence curve is very illustrative. The merits of a consideration of the temperature dependence of luminescence are not restricted, however, to the negative purpose of discarding useless products. A systematic study of the phenomenon may lead to an insight in its physical nature, enabling us to control it, or anyway giving indications for the improvement of luminophors on this point.

We give below a number of experimental data, followed by some theoretical considerations.

2. EXPERIMENTAL DATA

2.1 Reference to previous sections

Experimental data concerning the temperature dependence of luminescence are available for a considerable number of luminophors. In the preceding sections we have already reported experimental results regarding Mg_2TiO_4–Mn (Chapter II, Section 2.4.4, Fig. 13), β-Al_2O_3–Mn (Chapter II, Section 3, Fig. 22), tungstates and molybdates (Chapter III, Section 4, Fig. 27 and 28), $PbWO_4$–$(Ca$–Sr–$Ba)WO_4$ (Chapter III, Section 5, Fig. 31, 32), $Ca(W$–$Mo)O_4$ (Chapter III, Section 6), $CaWO_4$–Sm (Chapter III, Section 8, Fig. 41), uranium luminophors (Chapter IV, Fig. 43 and 44), and titanium luminophors (Chapter V, Section 5, Fig. 50, 51).

In the following we shall give a description of the temperature dependence of luminescence for some more systems.

2.2 Zinc sulphide luminophors

Data concerning zinc sulphide luminophors are to be found in the literature by GUNTZ [1], RANDALL [2], RIEHL [3], ROTHE and SCHÖN [4], UEHARA [5], BRAUER [6], ADDINK [7], GARLICK and WILKINS [8], and LEVERENZ [9]. As the results obtained by these authors are not always consistent we have repeated and extended these investigations.

Fig. 52 shows the temperature dependence of the blue
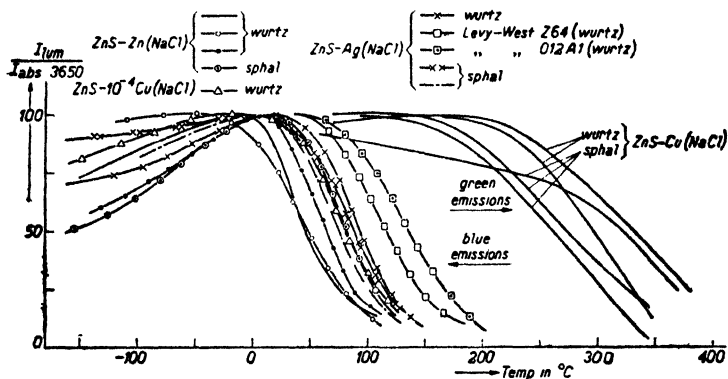
Fig. 52. Temperature dependence of the luminescence of zinc sulphide luminophors for excitation by λ 3650 Å.

emissions of *ZnS–Zn(NaCl)*, *ZnS–Ag(NaCl)* and *ZnS*–0.1 % *Cu(NaCl)*, and of the green emissions of *ZnS* containing a small amount of copper, both for the hexagonal wurtzite

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[1] A. A. GUNTZ, *Ann. chim.*, (10), **5** (1925) 363.
[2] J. T. RANDALL, *Proc. Phys. Soc. London*, **49** (suppl.), (1937) 46.
[3] N. RIEHL, *Ann. Phys.*, (5), **17** (1933) 587; (*Physik und techn. Anw. der Luminescenz*, Berlin, **1941**, p. 82).
[4] H. ROTHE–M. SCHÖN, *Verh. dtsch. phys. Ges.*, **20** (1939) 151. M. SCHÖN, *Naturw.*, **31** (1943) 169.
[5] Y. UEHARA, *J. Chem. Soc. Japan*, **60** (1939) 900 (in Japanese)
[6] P. BRAUER, *Naturw.*, **32** (1944) 32.
[7] N. W. H. ADDINK, D.R.P. 684.297.
[8] G. F. J. GARLICK–M. H. F. WILKINS, *Proc. Roy Soc. London A*, **184** (1945) 425.
[9] H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 199.

and the regular sphalerite modification. The luminescence was excited in the long wave-length extension of the fundamental absorption band by λ 3650 Å. For the measurements samples have been chosen in which centres of only one kind are present. For the blue luminescent system this condition was never completely fulfilled, all samples showing a green luminescence at high temperatures, but samples were chosen in which this green luminescence was faint compared to the blue emission.

On the whole the results obtained by RANDALL were confirmed. The blue emissions are quenched at a much lower temperature than the green ones. Differences in behaviour between wurtzite and sphalerite were only found for the blue emission of "unactivated" zinc sulphide, the wurtzite being quenched at a lower temperature than the sphalerite. For the other blue bands and for the green emissions such differences are not observed. If they exist they are overshadowed by variations in the quenching ranges due to other influences like the temperature at which the sample has been fired during preparation, the activator concentration, etc. The quenching ranges of the blue bands of *Ag* and *Cu* in both modifications and that of *Zn* in the sphalerite modification do not show larger differences than occur between different specimen of each. Together with the resemblance in the spectral distribution of the emissions, this suggests that the centres in which these bands originate are very much alike. In some cases in which the blue emission decreases towards low temperatures, a new ultra violet band could be detected at low temperatures. This band, with a maximum at about 3800 Å [1], increases when the blue band decreases; hence the increase of the one band and the decrease of the other one might be interrelated. Yet this cannot be the sole reason for the decrease of the blue, for in other cases the 3800 Å band is not found.

Fig. 53 shows the temperature dependence of the blue and

[1] This band must not be confused with the fundamental emission of ZnS which has a maximum at 3400 Å. The latter is not excited by λ 3650 Å .The origin of the 3800 Å band is still unknown.

green emission bands for two samples in which both kinds of centres are present together. The bands have been separated roughly by means of filters SCHOTT BG24 for the blue band,
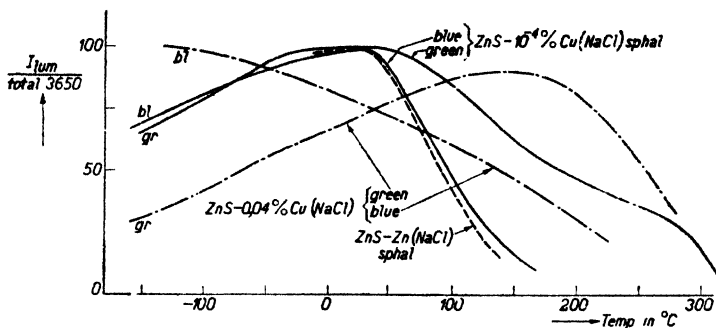
Fig. 53. Temperature dependence of the separate blue and green emission in two samples of *ZnS–Cu* together with the temperature dependence of the blue emission of unactivated *ZnS*. The bands have been separated by means of the SCHOTT filters BG24 and OG4.

OG4 for the green band. The curves are plotted in arbitrary units, the maxima of all having been fixed at the 100 level. The first sample is a zinc sulphide containing an extremely small amount of copper (10^{-4}%). The blue emission of this sample is obviously that of *ZnS–Zn(NaCl)*. It is quenched at the same temperature as was found for products containing no copper (Fig. 52). The green band is much more persistent [1].

The other sample is a zinc sulphide containing a high amount of copper (0.04%). Since a medium concentration of copper causes the occurrence of the well known green copper emission in place of the blue *ZnS–Zn(NaCl)* emission, the blue occurring at high copper concentrations [2] is probably also caused by the copper [3]. Also in this case the green emission is more

[1] Since the long-wave part of the blue band is transmitted by the green filter, the decrease of the green measured between 50 and 150° C is partly due to the decrease of the blue emission in this range.

[2] Cf. also S. T. HENDERSON, *Proc. Roy. Soc. London,*, (A) **173** (1939) 331.

[3] Obviously this same reasoning applies to the blue band of the sample of *ZnS–Cu* (0.01%), the temperature dependence of which is shown in Fig. 52.

persistent than the blue emission. The blue emission is quenched much more gradually than was found for the samples containing blue centres only. Since the green emission increases in the range in which the blue decreases, the blue band is probably replaced by the green band.
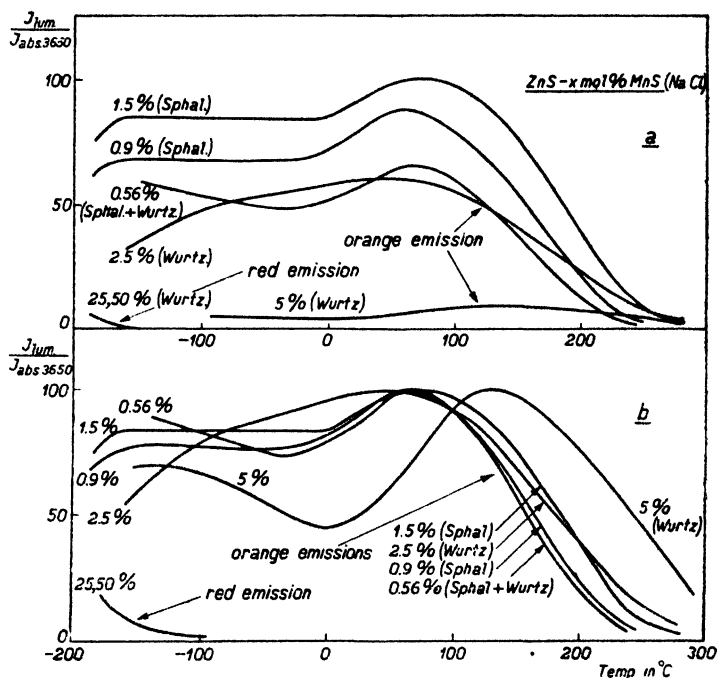
Fig. 54. Temperature dependence of the orange and red luminescence of *ZnS–MnS* (*NaCl*) of various manganese contents for excitation by λ 3650 Å.
a. true intensity ratios.
b. all maxima fixed at 100.

Our results with the emission of *ZnS–MnS*(*NaCl*) on excitation by λ 3650 Å are given in fig. 54; for the orange-yellow band they are in agreement with those obtained by Randall and by Guntz. Below —170° the efficiency increases with temperature; it remains constant from —170° up to 0° C and

then increases to a maximum value at 80° C. At a still higher temperature the efficiency decreases suddenly due to temperature quenching. The maximum is real and is certainly not due to a possible insufficient allowance for the variation of absorption [1]: it also occurs upon excitation with λ 2537 Å, the absorption of which does not change considerably with the temperature. With increasing manganese concentration the persistence of the orange-yellow emission increases slightly; the intensity decreases. The origin of this decrease is indicated by the occurrence of a red emission which, having a low quenching point is only observed at low temperatures [2]. At the temperatures at which it is quenched, the red emission mechanism constitutes a sort of leak through which the excitation energy is transferred to the lattice in the form of heat [3].

On excitation in the fundamental absorption of *ZnS* with $\lambda < 3400$ Å (Fig. 55, λ 2537 Å) the quenching of the orange-yellow *ZnS–Mn* emission sets in at a much lower temperature and increases slowly and gradually with increasing temperature up to the point where for λ 3650 Å excitation the abrupt fall of the intensity occurs. At this temperature the remaining part of the luminescence is quenched in the same rapid way. Obviously the quenching is now effected by two different, superposed mechanisms (cf. Section 4.4). On excitation in the characteristic bands of the manganese ions (λ 4047, 4358, 4917 Å), the same emission is emitted, but now it is far more persistent. As was observed visually, even up to 450° C no marked quenching occurs [4].

[1] The reflection for λ 3650 Å changes gradually from 45% at —100° C to 10% at +300° C, indicating a considerable variation of the absorption.

[2] F. A. KRÖGER, *Physica*, **6** (1939) 369, *Dissertation* Amsterdam, 1940, p. 45—46.

[3] Incidentally it may be emphasized that this "leak", together with the specific character of the phosphorescence (electrons from all metastable levels cause exclusively phosphorescence in the yellow band), offers an explanation for the discrepancy between the energy stored as obtained from the fluorescence-increase and the phosphorescence-decay curves (J. T. RANDALL–M. H. F. WILKINS, *Proc. Roy Soc., London,* **A 184** (1945) 403.

[4] Similar differences in persistence have been observed by GARLICK and WILKINS, *loc. cit.*

Differences between the temperature dependence of luminescence produced by excitation in the fundamental absorption band of the matrix lattice and in the long wave-length extension of this absorption — similar to those reported above
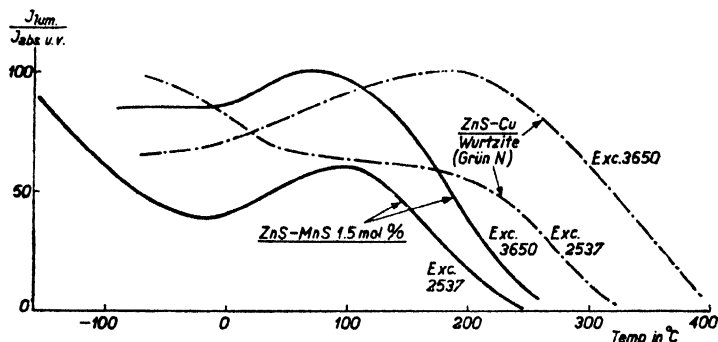
Fig. 55. Intercomparison of the temperature dependence of *ZnS* luminophors, excited by λ 3650 Å and 2537 Å (arbitrary units).

for *ZnS–MnS* (*NaCl*) — were found in *ZnS–Cu* (Fig. 55) and, according to measurements by ROTHE and SCHÖN (*loc. cit.*) occur probably also in (*Zn–Cd*)*S–Cu*, and in "unactivated" *ZnS* and (*Zn–Cd*)*S*.

It is remarkable, however, that such differences do not occur without exception. We found for instance the same temperature dependence with unactivated *ZnS–CdS* (30 mol %) excited by λ 3650 Å in the fundamental absorption or by λ 4358 Å in the long wave-length tail of this absorption. RIEHL [1], exciting *ZnS–Cu* by α-rays [2] found the same temperature dependence as was found by us for excitation by λ 3650 Å. It seems to be of interest to study the effect more closely.

All measurements which have been reported so far, have been carried out at a certain constant intensity of excitation.

[1] N. RIEHL, *Ann. Phys.*, (5), **17** (1933) 587.

[2] This method of excitation should be comparable with that effected by short-wave radiation.

Now RIEHL[1] has observed that in the temperature range in which the green and blue bands of *ZnS–Cu*, *ZnS–Ag* and *ZnS–CdS* are quenched, the efficiency of the luminescence is dependent on the intensity of the exciting radiation, a high intensity of excitation giving a high efficiency. This means that the quenching range itself is dependent on the intensity of excitation, an increase of this intensity of excitation causing it to shift towards higher temperatures. We have repeated the experiments with blue luminescent *ZnS–Ag* and green
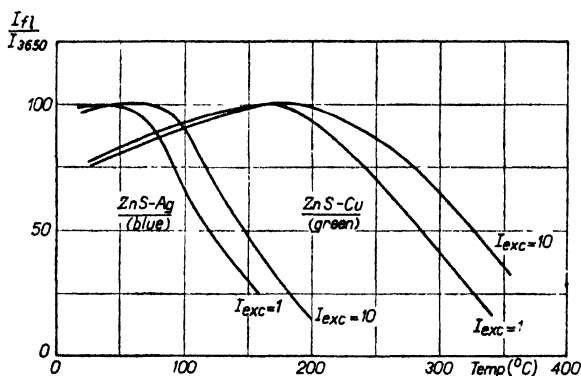
Fig. 55A. Temperature dependence of the luminescence for *ZnS–Cu* and *ZnS–Ag* for different intensities of the exciting λ 3650 Å radiation.

luminescent *ZnS–Cu*, exciting the samples by two intensities of λ 3650 Å radiation, one of which was ten times as high as the other. The results as given in Fig. 55A show very clearly the effect mentioned above. An increase of the intensity of the exciting radiation by a factor ten causes the quenching range to shift over $\sim 50°$ C for *ZnS–Ag*, $\sim 40°$ for *ZnS–Cu*. Recently the effect has also been observed by URBACH c.s.[2].

According to LEVERENZ[3] the quenching points of cathodo-

[1] N. RIEHL, *Z. techn. Phys.*, **20** (1939) 152; *Phys. u. techn. Anw. Lumineszenz*, Berlin 1941, p. 117.
[2] F. URBACH–A. URBACH–M. SCHWARTZ, *J. Opt. Soc. Am.*, **37** (1947) 122.
[3] H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 237.

luminescence are about 100–150° C higher than those of the corresponding luminescence excited by ultra violet. This may well be also an intensity effect, cathode rays being absorbed in a very thin surface layer.

2.3 $Cd_2B_2O_5$–$Mn_2B_2O_5$

The temperature dependence of the orange luminescence of $Cd_2B_2O_5$–Mn was measured for excitation by λ 2537 Å
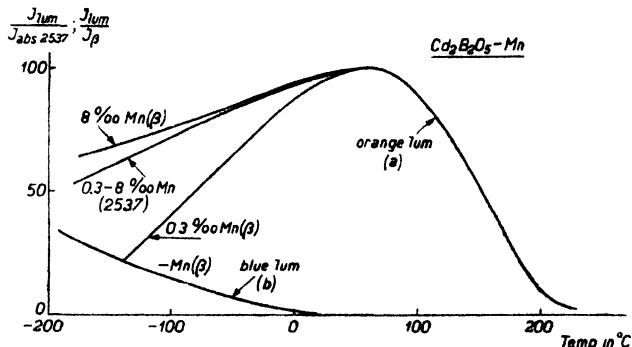
Fig. 56. Temperature dependence of the orange luminescence of $Cd_2B_2O_5$–Mn for products of various manganese contents. Excitation by λ 2537 and cathode rays (β).

and by cathode rays (Fig. 56). The quenching which sets in at 60° C and is completed at 200° C, is identical for various activator concentrations and different methods of excitation [1]. From 60° downwards the intensity decreases, as was already observed by DINGER and KUNERTH [2], and LEVERENZ [3] For excitation by β-rays this decrease is dependent on the manganese concentration, the sharpest fall being found with the products containing the smallest amount of activator. A

[1] An increase of the persistence by the introduction of zinc into the crystals, as reported in NETH. PAT. 96.980; U.S.A. PAT. SPEC. 2.316.366; D.R.P. 704.086 could not be reproduced.

[2] J. E. DINGER–W. KUNERTH, *Iowa State College J. Sc.*, **14** (1940) 195.

[3] H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 199.

faint ultra violet luminescence of unknown origin occurring particularly with $Cd_2B_2O_5$ containing very little manganese is found next to the manganese emission with an intensity which decreases with increasing manganese content. As this emission is quenched in the temperature range in which the manganese emission increases, both phenomena might be coupled. The intensity of the ultra violet band, however, is so low that a transfer of energy from the u.v. to the orange band cannot account for the total increase of the latter. Moreover the increase of the manganese emission, excited by λ 2537 Å, is nearly independent of the manganese concentration, while as we saw already the intensity of the u.v. emission is markedly dependent on it. Therefore another explanation has to be sought [1].

2.4 $CdSiO_3$–$MnSiO_3$

Fig. 57 shows the temperature dependence of the intensity of the orange luminescence of $CdSiO_3$–*Mn* upon excitation by 2537 Å and cathode rays. The part of the curves above 60–100° C indicates a slight decrease of persistence with increasing manganese content. Below 60° C the curves show a decrease towards lower temperatures to an extent which is equally dependent on the manganese concentration. For products containing 1 mol % *Mn* or more, the intensity only decreases slightly; for samples containing 0.1 mol %, and still more for those containing 0.01 mol % *Mn*, the decrease is rather steep. This decrease cannot be caused by a variation in the absorption, 2537 Å being absorbed in the fundamental absorption band, almost independently of the temperature from 0 to 300° C, the reflection varying only from 30 to 15%. Similar effects occur on excitation by cathode rays in which case a variation can certainly be excluded. A clue to the solution of this problem is possibly provided by a blue luminescence occurring at low temperatures. This luminescence, which may be due to traces of an additional contamination, occurs particularly with unactivated $CdSiO_3$, but with a smaller intensity also with the

[1] TH. P. J. BOTDEN–F. A. KRÖGER, *Physica,* **13** (1947) **216.**
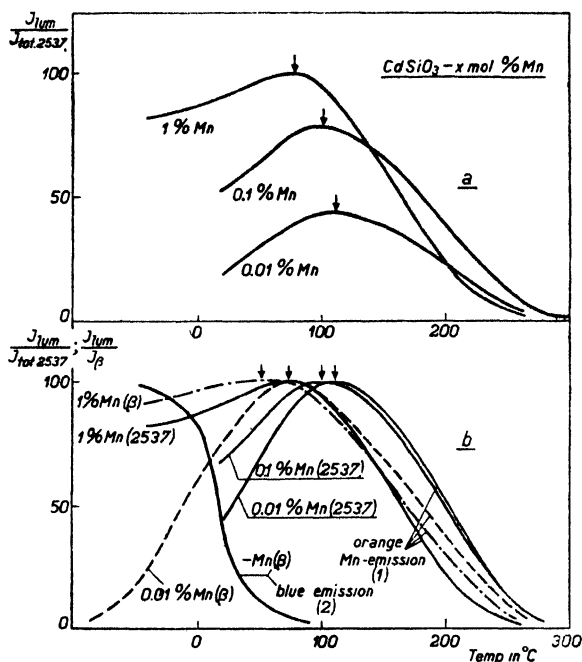
Fig. 57. Temperature dependence of the luminescence of *CdSiO₃–Mn*.

a. orange manganese emission; true intensity ratios for excitation by λ 2537 Å.

b. all maxima fixed at 100.

(1) orange manganese emission; excitation by λ 2537 Å or β-rays.

(2) blue emission of unactivated $CdSiO_3$; excited by β-rays.

products containing manganese. The temperature dependence of this emission, equally shown in Fig. 57, reveals that quenching occurs in the same range in which the manganese emission increases. This suggests the existence of a correlation between these two phenomena, a situation similar to the one suggested in the previous section for $Cd_2B_2O_5$–*Mn*. Yet, the intensity of the blue band seems to be too low to allow the assumption of a simple substitution of the blue band by the orange band. Quantitative measurements are required to

give a conclusive answer to this question, but probably a different explanation has to be sought also in this case.

2.5 CdI_2

Fig. 58 shows the temperature dependence of various emissions occurring with CdI_2. A green emission of CdI_2–$MnCl_2$, which is also found with pure CdI_2, only appears at low temperatures and is already totally quenched at room temperature. A yellow-orange emission of CdI_2–Pb is a little more persistent [1],
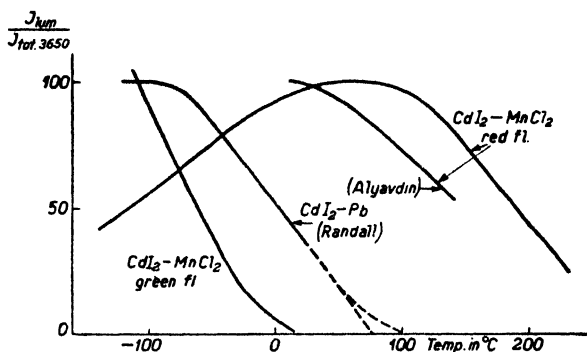
Fig. 58. Temperature dependence of the luminescence of *CdI* in various bands.

while the red manganese emission of CdI_2–$MnCl_2$ is quenched at a considerably higher temperature. The results by ALYAVDIN c.s. [2] which differ slightly from ours, are also shown in Fig. 58. Intercomparison of the curves of the green and the red emission of CdI_2–$MnCl_2$ reveals the nature of the phenomenon of colour variation, as first described by RANDALL [3]. In the temperature range in which the green band is quenched, the red emission appears instead.

When our experiments had been completed, we became

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[1] This curve has been taken from the paper by J. T. RANDALL, *Proc. Phys. Soc. London*, **49** (suppl.) (1937) 46.

[2] V. N. ALAYVDIN–V. V. FEDOROV–V. L. LEWSCHING, *C.R. acad. sc. U.R.S.S.*, **25** (1939) 106, ref. *Chem. Abstr.*, **34** (1940) 3593.

[3] J. T. RANDALL, *Trans. Far. Soc.*, **35** (1939) 12.

acquainted with recent work by GARLICK and WILKINS[1]. As far as their experiments coincide with ours, the agreement is satisfactory. These authors observed further a difference between the temperature dependence of the CdI_2 emission on excitation by λ 3650 Å and λ 2537 Å, the temperatures of complete quenching being 0° C and 50° C respectively.

2.6 Zn_2SiO_4–Mn_2SiO_4 and $(Zn–Be)_2SiO_4$–Mn_2SiO_4

According to FONDA and ZENER[2] the temperature dependence of Zn_2SiO_4–Mn_2SiO_4 is a function of the manganese
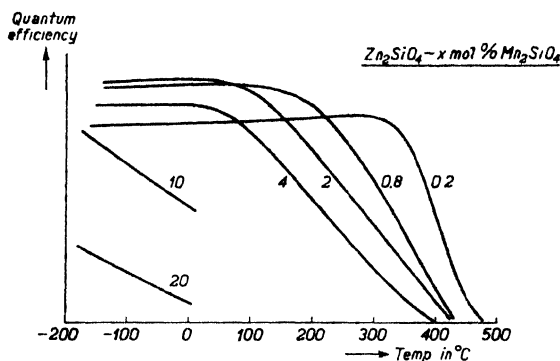
Fig. 59. Temperature dependence of the quantum efficiency of the luminescence of $Zn_2SiO_4 - x$ mol % Mn_2SiO_4, according to FONDA and ZENER, (R. P. JOHNSON, *Am. J. Phys.*, **8** (1940) 143).

concentration (Fig. 59). For excitation by λ 2537 Å in the Mn_2SiO_4 absorption, the luminescence of products containing 0.2 mol % Mn_2SiO_4 or less is constant up to about 300° C and decreases rather sharply towards higher temperatures. For higher manganese contents the persistence diminishes; at the same time the slope of the intensity versus temperature curves decreases.

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[1] G. F. J. GARLICK–M. H. F. WILKINS, *Proc. Roy. Soc. London*, **A 184** (1945) 425.

[2] R. P. JOHNSON, *Am. J. Phys.*, **8** (1940) 143.
G. R. FONDA, *J. Phys. Chem.*, **43** (1939) 561.

The flat shape of the quenching curves may be explained by the complexity of the emission spectra. For Zn_2SiO_4–0.1 mol % Mn_2SiO_4 the emission consists almost exclusively of one green band; at higher manganese concentrations this band is displaced somewhat towards longer wave-lengths, and at least one more (red) band appears in addition [1].

Separating the red and the green bands roughly with the aid of filters (viz., SCHOTT BG 23 and RG 1) we have deter-
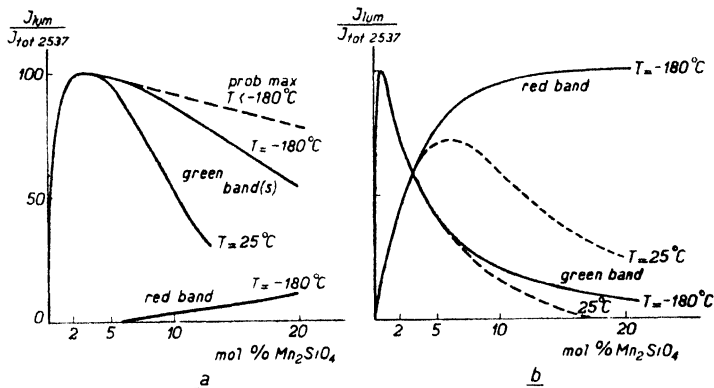
Fig. 60. Intensity of the green and red emission bands of zinc silicate-*Mn* and zinc beryllium silicate-*Mn* for excitation by λ 2537 Å as a function of the manganese content.
a. $Zn_2SiO_4 - x$ mol % *Mn*.
b. $(Zn - 15$ mol % $Be)_2SiO_4 - x$ mol % *Mn*.

mined the intensity of both bands. Fig. 60*a* shows the results for products of various manganese content. For the products of high manganese content where even at —180° the maximum intensity is not yet reached, the probable value of the maximum intensities to be reached at still lower temperatures are estimated from the shape of the quenching curve. The maximum intensity of the green band increases with the manganese content in the region of low concentrations, then becomes nearly constant and finally drops slightly in the region above 5

[1] F. A. KRÖGER, *Physica*, **6** (1939) 764; *Dissertation*, Amsterdam, 1940, p. 18; J. H. SCHULMAN, *J. Appl. Phys.*, **17** (1946) 902.

mol % where the red band appears to a measurable extent.

In the zinc-beryllium silicates (Fig. 60*b*) [1] the situation is similar, the only difference being that the red emission is favoured; it appears at much smaller manganese concentrations and is emitted almost without admixture of the green band in products containing a high amount of manganese, i.e., with a content of 15 mol % *Be* and 30 mol % *Mn* or more [1].

For each sample the temperature dependence of the red and the green sub-band is different, the green band being the most persistent one under all circumstances [2]. With *Zn–Be* silicates of varying composition the quenching temperatures of both sub-bands vary gradually with the manganese content, decreasing towards higher concentrations probably as a consequence of the variation of the over-all properties of the mixed crystals (Fig. 61*b*). With Zn_2SiO_4–*Mn* the situation is somewhat more complicated; besides the lowering of the
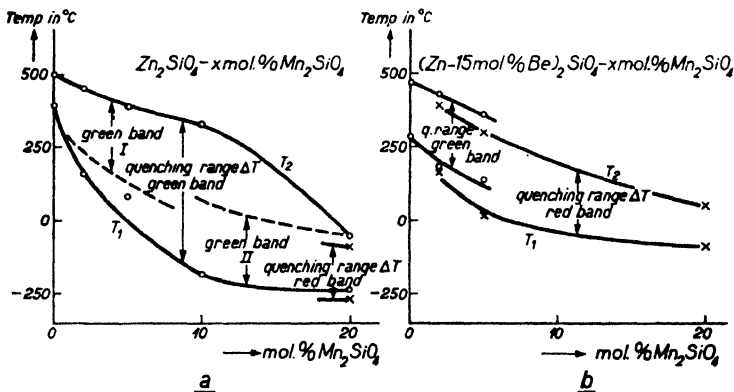
Fig. 61. Temperatures of the beginning and ending of temperature-quenching for the red and green sub bands of zinc silicate-*Mn* (*a*) and zinc beryllium silicate-*Mn* (*b*), as a function of the manganese content.

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[1] Our results are in agreement with those obtained by K. Birus, *Ergebn. Exakt. Naturw.*, **20** (1942) 211.

[2] A similar phenomenon has been observed with glasses activated by manganese.
S. H. Linwood–W. A. Weyl, *J. Opt. Soc. Am.*, **32** (1942) 443.

quenching temperature of the green band, the quenching range of this emission is widened considerably (Fig. 61*a*). This suggests that the measured green emission is not a single band, but consists of at least two bands of only slightly different spectral distribution. The reported "shift" of the green emission upon variation of the manganese content may also be explained in this way. In Fig. 61*a* the separate quenching ranges of two supposed green sub-bands are marked by dotted lines.

The emissions excited by λ 3650 Å or 4358 Å in the characteristic absorption bands of the divalent manganese ions, which have the same spectral distribution as those excited by λ 2537 Å, are also quenched in exactly the same temperature range as these emissions. So obviously the quenching occurs by the same mechanism in both cases.

The various sub-bands must be correlated with electron transitions in manganese ions under different conditions. According to LINWOOD and WEYL (*loc. cit.*) and SCHULMAN (*loc. cit.*) the green emission is due to manganese ions surrounded by four oxygen ions (Mn^{2+} at Zn^{2+} positions), the red emission due to manganese surrounded by six oxygen ions (Mn^{2+} at interstitial positions). However the presence of divalent manganese at interstitial positions is not very probable [1]. Besides, this picture does not account for the essential influence of the manganese concentration. We prefer a picture in which the manganese is placed at normal lattice positions, the different configurations consisting of manganese ions with none, one, two or more other manganese ions at neighbouring zinc positions. The beryllium may either affect the manganese directly in the same way as the other manganese ions by changing the symmetry of the electric field [2], or it may

[1] At the end of their paper, LINWOOD and WEYL introduce a different picture in which the configuration formed by manganese and its surroundings is affected in its temperature motion. Although this factor may well have influence on the temperature dependence of the emission, it is hardly conceivable that it should affect the spectral distribution more than by causing a slight additional broadening.

[2] K. BIRUS, *Ergebn. Exakt Naturw.*, **20** (1942) 212.

increase the clustering of manganese ions, thus causing the occurrence of groups of two, three or more manganese ions at concentrations at which most of the manganese ions in Zn_2SiO_4–Mn_2SiO_4 are still isolated.

It remains open to question whether the different transitions take place between corresponding levels, modified by the influence of the surroundings, or whether they occur between totally different levels which exist in each manganese ion, while only the relative transition probabilities for the various transitions are changed. Probably both possibilities are realized.

The temperature dependence has also been determined for excitation with cathode rays. According to MOSKWIN [1] the quenching ranges are the same as for excitation with ultra violet. LEVERENZ [2] on the other hand reports that the quenching point of cathodo-luminescence is 100–150° C higher than that of luminescence excited with ultra violet. If we study the curves given by MOSKWIN it is seen that, in spite of the author's comment, differences between the quenching ranges occur which are of the same magnitude as those reported by LEVERENZ. Our own measurements show the same result. Therefore the effect seems to be real. It resembles a similar effect in ZnS luminophors. In Section 2.2, it has already been supposed that such effects are essentially due to variation in excitation intensity. We have actually been able to find such an intensity effect with Zn_2SiO_4-Mn excited with λ 2537 Å. An increase of the exciting intensity with a factor ten caused the quenching range to shift over 10–15° C towards higher temperatures.

The correspondence with ZnS goes still further if we consider the influence of iron. As has recently been observed "killers" present in ZnS cause a decrease of the quenching temperature [3]. A similar effect has already been reported for iron in Zn_2SiO_4–Mn by ZENER [4]. Repeating these experiments we have been able to confirm this result (Fig. 62). The decrease of the in-

[1] A. V. MOSKWIN, *Bull. acad. Sci., U.R.S.S.*, sér. phys., **9**, (1945) **467**, ref. *Chem. Abstr.*, **40** (1946) **4606**.
[2] H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) **199**.
[3] H. A. KLASENS, *Nature*, **158** (1946) **306**.
[4] C. ZENER, cited by G. R. FONDA, *J. Phys. Chem.*, **43** (1939) **561**.

tensity of Zn_2SiO_4-Mn caused by iron is due to two effects. The first diminishing effect is independent of the temperature and is caused by a competing ineffective absorption. The second effect consists of a change in the temperature dependence, causing a decreasing persistence with an increasing iron
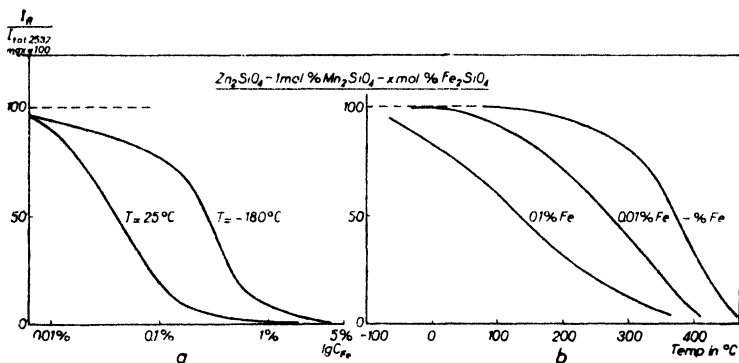
Fig. 62. Quenching effect of iron on the luminescence of Zn_2SiO_4 — 1 mol % Mn_2SiO_4.

a. intensity for excitation by λ 2537 Å at 25° and —180° C (arbitrary units).

b. temperature dependence of the intensity for 0, 0.1 and 0.01 mol % Fe_2SiO_4 (maxima put equal to 100).

concentration together with a broadening of the quenching range. It is remarkable that considerable effects occur with iron concentrations as low as 0.01–0.1 of that of the manganese (0.1–1°/₀₀ *Fe* in Zn_2SiO_4 containing 1 mol % Mn_2SiO_4).

Just like the killers in *ZnS*, the iron in Zn_2SiO_4-Mn suppresses particularly the phosphorescence, even in systems in which many traps are present (Zn_2SiO_4-Mn-As) [1].

2.7 Al_2O_3-Cr_2O_3

The temperature dependence of Al_2O_3-Cr was measured by RANDALL [2]. The situation is complicated by a variation of the emission spectrum, high temperatures favouring a broad

[1] W. HOOGENSTRAATEN, private communication.

[2] J. T. RANDALL, *Proc. Phys. Soc. London*, **49** (suppl.) (1937) 46.

and diffuse orange emission at the cost of the well-known sharp doublet in the red.

2.8 Silicates with Ce

In Fig. 63 and 64 the temperature dependence of the blue luminescence of trivalent cerium in various silicates excited
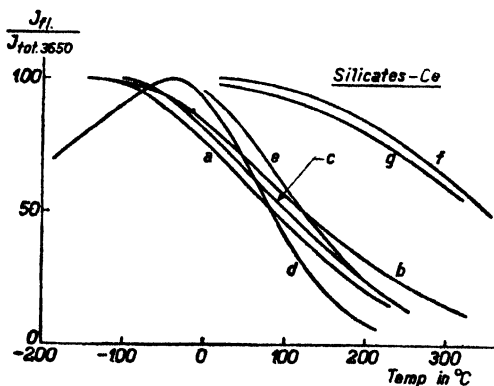
Fig. 63. Temperature dependence of the luminescence of various silicates activated by trivalent cerium for excitation by λ 3650 Å (maxima put equal to 100).

a. Be_2SiO_4 – 0.05 mol Ce_2O_3
b. $Ca_2Al_2SiO_7$ – x mol Ce_2O_3
c. $CaAl_2Si_2O_8$ – 0.03 mol Ce_2O_3
d. Na_2SiO_3 – 0.05 mol Ce_2O_3
e. $Al_3Si_2O_{13}$ – 0.3 mol Ce_2O_3
f. $Ca_3Si_2O_7$ – 0.1 mol Ce_2O_3
g. $Sr_3Si_2O_7$ – 0.05 mol Ce_2O_3

by λ 3650 or 2537 in the cerium absorption bands are shown, as determined by OVERBEEK [1]. For lanthanium silicate the temperature dependence is dependent on the cerium concentration, the intensity-temperature curves becoming less steep with an increase in cerium content (Fig. 64). As it is known that the spectra of cerium luminophors are usually complex [2], these effects may be explained on this basis, assuming that the emission is built up of various sub-bands of different

[1] J. TH. G. OVERBEEK, private communication.
[2] F. A. KRÖGER–J. BAKKER, *Physica*, 8 (1941) 628.

quenching behaviour, the sub-bands with the smallest persistance being favoured by high activator contents. As Ce^{3+}
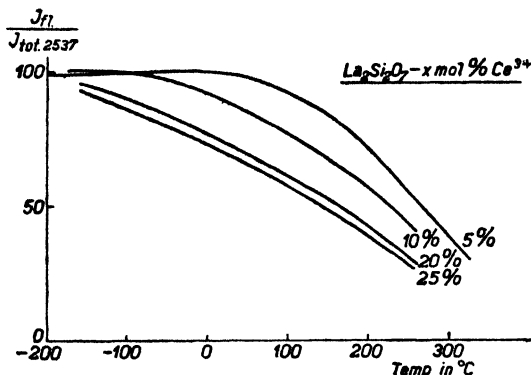
Fig. 64. Temperature dependence of the luminescence of $La_2Si_2O_7$–Ce excited by λ 2537 for various cerium contents.

is nearly identical with La^{3+} in practically every respect, we must expect that the quenching of each sub-band is not changed. Indeed, in agreement with this, the temperature of complete quenching, which is determined by the sub-band of the greatest persistence, hardly changes upon variation of the composition.

2.9 Glasses, activated by Mn, Ce, Sn and Cu.

Fig. 65, 66 and 67 show the temperature dependence of the luminescence of some luminescent glasses according to Overbeek. Fig. 65 applies to glasses activated by tin, Fig. 66 to a calcium phosphate glass activated by tin and (or) manganese. The latter system offers another example of two different emissions taking place in the same matrix substance without interfering: the temperature dependence of the separate emission bands due to *Sn* and *Mn* is the same for the glasses containing these activators together and for those containing only one of them.

Fig. 67 shows the effect of crystallization on the temperature dependence of calcium phosphate activated by cerium. Although the crystallization induced by annealing the glass for 3 hours
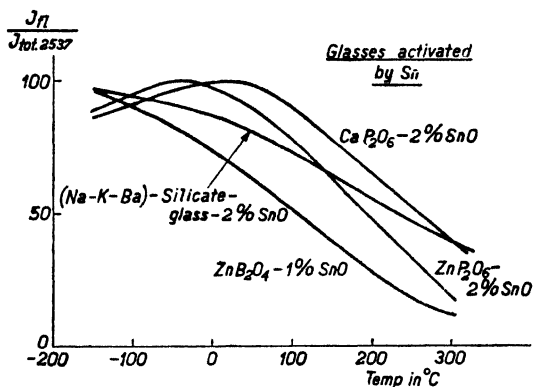
Fig. 65. Temperature dependence of the luminescence of glasses activated by tin, for excitation by λ 2537 Å.

at 750° C may not be complete, the temperature dependence is markedly changed and tends to become steeper.

RODRIGUEZ c.s.[1] investigated the temperature dependence
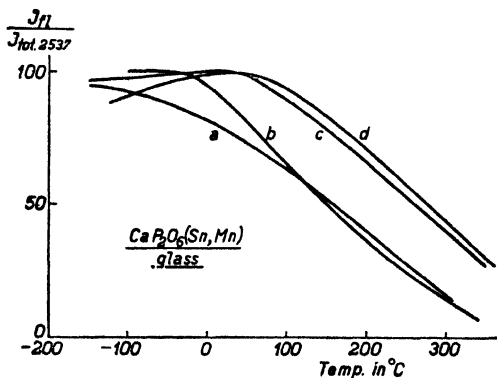
Fig. 66. Temperature dependence of the luminescence of calcium phosphate glass activated by tin and/or manganese in the separate emission bands:

a. CaP_2O_6 – 6% *Mn* , orange emission.
b. CaP_2O_6 – 6% *Mn*+2% *Sn*, orange emission.
c. CaP_2O_6 – 6% *Mn*+2% *Sn*, blue emission.
d. CaP_2O_6 – 2% *Sn* , blue emission.

[1] A. R. RODRIGUEZ–C. W. PARMELEE–A. E. BADGER, *J. Am. Cer. Soc.*, **26** (1943) **137**.

of the blue and red emission of glasses activated by tin and atomic copper. The intensity increases from low temperatures up to ~ 100°, passes through a maximum and decreases again at higher temperatures.
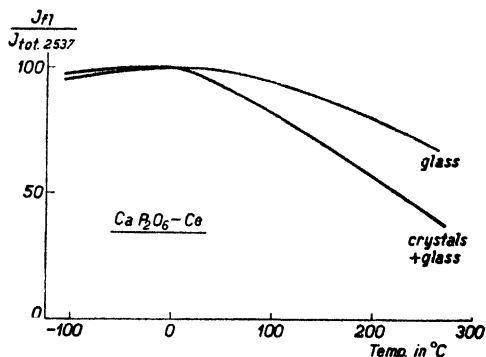
Fig. 67. Temperature dependence of the blue luminescence of CaP_2O_6 activated by cerium in the glass state and in a more or less purely crystalline state for excitation by λ 2537.

LINWOOD and WEYL [1], studying glasses activated by manganese, report the occurrence of phenomena very similar to the ones described above for the zinc-beryllium silicates (Section 2.6). The emission consists of green and red sub-bands which behave differently and independently with respect to temperature. The green band is most persistent, its quenching starting above 200° C. The quenching range of the red band extends from below room temperature up to about 100° C.

2.10 CaO

NICHOLS and WILBER [2] observed that a sample of *CaO* which was non-luminescent at room temperature showed a red and green cathodo-luminescence at higher temperatures. The intensity of the red band increased up to 300° C, passed through a maximum there, and decreased to be totally quenched

[1] S. H. LINWOOD–W. A. WEYL, *J. Opt. Soc. Am.*, **32** (1942) 447.
[2] E. L. NICHOLS–D. T. WILBER, *Phys. Rev.*, **17** (1921) 707.

at 600° C. The green band increased up to 430° C and was totally quenched at 720° C.

2.11 Miscellaneous

AB[1] has measured the temperature dependence of the fluorescence of Zn_2SiO_4–Nb and ZnB_4O_7–Mn. The quenching range of the first system extends from 100–300° C. ZnB_4O_7–Mn behaves more complicated, similar to $Cd_2B_2O_5$–Mn. Below room temperature the fluorescence increases with increasing temperature. Above room temperature quenching sets in, which is completed in an abnormally wide range extending from 20–500° C.

According to LEVERENZ[2] the temperature dependence of Zn_2GeO_4–Mn is like that of Zn_2SiO_4–Mn. This author measured also ZnO–Zn, ZnS, ZnS–CdS and ZnS–$ZnSe$ luminophors.

KOMOVSKY and GOLOVCHINER[3] have studied the temperature dependence of a number of minerals, viz., quartz, rutile, realgar, scheelite, wollastonite, amethyst, muscovite, monazite, orpiment (oripigment?), uranium minerals, arsenic minerals, etc. According to the summary as given in *Chem. Abstr.*, the latter three show the phenomenon of decrease of intensity towards lower temperatures. Since we have not been able to get hold of the original publication, details cannot be given.

LASHKAREV and KOSSONOGOVA[4] measured the temperature dependence of the infra red luminescence of Cu_2O, and found an increase towards low temperatures. BOSE[5] reports about $NaCl$, KCl, $NaBr$, KBr, pure and with addition of copper, and about uranyl nitrate, naphtalene and anthracene.

2.12 Survey of the experimental data

The curves giving the efficiency of luminescence as a function of the temperature generally resemble one of the three curves drawn in Fig. 68.

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[1] E. A. AB, *Bull. acad. sci. U.R.S.S.*, sér. phys., **9** (1945) 467.
[2] H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 199.
[3] G. F. KOMOVSKY–YA. GOLOVCHINER, *Sovjet. Geol.*, **8** (1940) 98, ref. *Chem. Abstr.*, **38** (1944) 701.
[4] V. E. LASHKAREV–K. M. KOSSONOGOVA, *C.R.* (*Doklady*) *U.R.S.S.*, **54** (1946) 125.
[5] H. N. BOSE, *Ind. J. Phys.*, **20** (1946) 21.

TABLE XXIV

No.	Luminophor	No. of figure	Excitation	Type of excitation*	T_1 (°C)	T_2 (°C)	ΔT	$T = \frac{T_1+T_2}{2}$ (°K)	$\frac{\Delta T}{T}$	Remarks	No.
1	$Cd_2B_2O_5$–Mn	56	2537, β	B, C	95	210	115	425	0.27		1
2	$CdSiO_3$–Mn	57	2537, β	C	135	265	130	473	0.28		2
3	Ca–β-Al_2O_3–Mn^{4+}	22	3650	A	5	105	100	333	0.30	red band	3
4	Ca–β-Al_2O_3–Mn^{2+}	22	β	C	260	460	200	633	0.32	green band	4
5	Sr–β-Al_2O_3–Mn^{2+}	22	β	C	300	540	240	693	0.35		5
6	Ba–β-Al_2O_3–Mn^{2+}	22	β	C	380	600	220	763	0.29		6
7	Mg_2TiO_4–Mn^{4+}	13	3650	A	90	200	110	418	(0.26)	strong, sharp red luminescence	7
8	Mg_2TiO_4–$Mn^{2+}+Mn^{4+}$	13	3650	A	−50	150	200	323	(0.62)	faint, diffuse red luminescence	8
9	Zn_2SiO_4–1°/₀₀ Mn^{2+}	59, 61	2537	B	390	445	55	690	0.08	green band	9
10	Zn_2SiO_4–10% Mn^{2+}	59, 61	2537	B	−180	370	550	368	(1.5)	superposition of some green bands?	10
11	$(Zn$–15% $Be)_2SiO_4$ — 2% Mn	61	2537	B	200	430	230	588	0.39	green band	11
			2537	B	160	390	230	548	0.42	red band	
12	$(Zn$–15% $Be)_2SiO_4$ — 20% Mn	61	2537	B	−90	50	140	253	0.55	red band	12
13	CdI_2–$MnCl_2$	58	3650	C	110	270	160	463	0.35	orange Mn-band	13
14	CdI_2–$MnCl_2$	58	3650	A	−130	0	130	208	0.63	green CdI_2-band	14
15	CdI_2–Pb	58	3650	C	−80	75	155	271	0.57	yellow Pb-band	15
16	ZnS–0.5% MnS $(NaCl)$ sphal.	54	3650	B	95	225	130	433	0.30		16
17	ZnS– 5% MnS $(NaCl)$ wurtzite	54	3650	B	160	320	160	513	0.31		17
18	ZnS–Cu sphal.; wurtzite	52	3650	A	190	370	180	553	0.33	green band	18
19	ZnS–Cu $(NaCl)$ wurtzite	52	3650	A	35	126	91	353	0.26	blue band	19
20	ZnS–Ag sphal.	52	3650	A	45	150	105	370	0.28		20
21	ZnS–Ag wurtzite	52	3650	A	20	90	70	328	0.21		21
22	ZnS–Zn $(NaCl)$ sphal.	52	3650	A	40	150	110	368	0.30		22
23	ZnS–Zn $(NaCl)$ wurtz.	52	3650	A	10	85	75	320	0.23		23
24	ZnS–CdS 35%, wurtz.	—	3650	C	20	120	100	343	0.29		24
25	ZnS–CdS–Cu, wurtz.	—	3650	C	50	290	240	443	0.54	GUNTZ, RANDALL	25
26	$SrWO_4$	27	2537	A	−180	5	185	185	1.—		26
27	Li_2WO_4	27	2537	A	−155	5	160	198	0.81		27
28	Ca_3WO_6	27	2537	A	−130	−20	110	198	0.56		28
29	$PbWO_4$	27	2537	A	−115	−15	100	208	0.48	blue band	29
30			3130	A	−70	80	150	278	0.54	green band	30
31	$Na_2W_2O_7$	27	2537	A	−65	15	80	248	0.32		31
32	$ZnWO_4$	27	2537	A	5	100	95	325	0.28		32
33	$CaWO_4$	27	2537	A	−5	135	140	338	0.41		33
34	$CdWO_4$	27	2537	A	45	145	100	368	0.27		34
35	$MgWO_4$ (β)	27	2537	A	45	185	140	388	0.36		35
36	$CaMoO_4$	28	2537	A	−65	75	140	278	0.50		36

* A is excitation in the centre
B ,, ,, ,, ,, activator compound
C ,, ,, ,, ,, matrix lattice

TABLE XXIV (continued)

No.	Luminophor	No of figure	Excitation	Type of excitation*	T_1 (°C)	T_2 (°C)	ΔT	$T = \frac{T_1+T_2}{2}$ (°K)	$\frac{\Delta T}{T}$	Remarks	No
37	$CdMoO_4$	28	2537	A	125	12	137	217	0.63		37
38	$Na_2Mo_2O_7$	28	2537	A	104	—20	84	211	0.40		38
39	$CdWO_4$–U	43	3650	A	70	50	120	263	0.46		39
40	Sr_2WO_5–U	43	3650	A	–45	75	120	288	0.42		40
41	Uranium glass	43	3650	A	80	150	230	308	0.75		41
42	$UO_2(NH_3)_3F_6$	43	3650	A	65	145	80	378	0.21		42
43	$MgSiO_3$–1% Ti	50	β	C	295	540	245	691	0.35		43
44	$SrSiO_3$–10% Ti	50	β	C	268	500	232	657	0.35		44
45	$CaSiO_3$–10% Ti	50	β	C	85	267	182	449	0.40		45
46	$(Ca$–$Mg)SiO_3$–1% Ti	50	β	C	175	420	245	570	0.43		46
47	Ca_2SiO_4–1% Ti	50	β	C	34	200	166	390	0.42		47
48	$CdSiO_3$–10% Ti	50	2537	C	20	160	140	363	0.39		48
49	Zn_2SiO_4–1% Ti	50	β	C	128	270	142	473	0.30		49
50	$Na_2Si_2O_5$–1% Ti	50	β	C	114	255	141	458	0.31		50
51	$Li_2Si_2O_5$–5% Ti	50	β	C	260	460	200	633	0.31	blue emission	51
			2537	A	140	70	210	238	0.89	green emission	
52	Mg_2SnO_4–1% Ti	51	2537	A	165	300	135	505	0.27		52
53	Ca_2SnO_4–1% Ti	51	2537	A	5	200	195	375	0.52		53
54	Sr_2SnO_4–1% Ti	51	2537	A	—60	180	240	333	0.72		54
55	$MgSnO_3$–10% Ti	51	2537	A	140	+160	300	373	(0.8)	superposition of $Sn+Ti$ bands	55
56	$CaSnO_3$–10% Ti	51	2537	A	200	20	220	183	1.2		56
57	$SrSnO_3$–10% Ti	51	2537	A	–240	—40	200	133	1.5		57
58	ZrO_2–1°/∞ Ti	51	2537	C	—5	135	140	338	0.41		58
59	$La_2Si_2O_7$–5% Ce_2O_3	64	2537	A	110	420	310	538	0.58		59
60	Be_2SiO_4–5% Ce_2O_3	63	3650	A	–80	270	350	368	0.95		60
61	$Ca_2Al_2SiO_7$–? Ce_2O_3	63	3650	A	–70	350	420	413	1.02		61
62	$CaAl_2Si_2O_8$–3% Ce_2O_3	63	3650	A	–70	280	350	378	0.93		62
63	Na_2SiO_3–5% Ce_2O_3	63	3650	A	–10	190	200	363	0.55		63
64	$Al_6Si_2O_{13}$–0.3 mol Ce_2O_3	63	3650	A	0	270	270	408	0.66		64
65	CaP_2O_6–6% MnO (glass)	66	2537	A	–20	340	360	433	0.83		65
66	CaP_2O_6–2% SnO (glass)	65, 66	2537	A	60	450	390	528	0.74		66
67	ZnP_2O_6–2% SnO (glass)	65	2537	A	20	360	340	463	0.73		67
68	ZnB_2O_4–1% SnO (glass)	65	2537	A	-120	330	450	378	1.2		68
69	Silicate glass — 2% SnO	65	2537	A	—70	530	600	503	1.2		69

* A is excitation in the centre
B ,, ,, ,, ,, activator compound
C ,, ,, ,, ,, matrix lattice

The temperature range inside which the luminescence decreases with the temperature is called the quenching range. Because of the shape of the curves it is rather difficult to point out unambiguously the temperatures at which the quenching sets in and at which it is completed. Therefore these temperatures T_1 and T_2 have been arbitrarily defined as the points of intersection of a straight line drawn through the points at which the intensity has fallen to 80% and 20% of the maximum value, with horizontal lines drawn at the
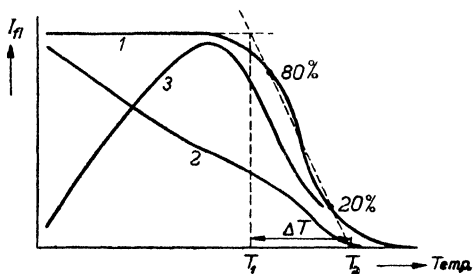
Fig. 68. Three types of temperature dependence of luminescence.

100% and 0% levels (cf. Fig. 68). The quenching range is correspondingly defined as the difference ΔT between these temperatures ($\Delta T = T_2 - T_1$).

In Table XXIV the temperatures T_1 and T_2 and the quenching range ΔT for all the emissions studied are given. T_1 varies from low temperatures up to temperatures above 400° C. It is different not only for the emissions due to one and the same activator in various matrix lattices (e.g., tungstates, molybdates, titanium luminophors, manganese luminophors), but also for the emissions of different activators in one and the same matrix lattice.

For instance, with β-Al_2O_3 the quenching temperature T_1 of the red Mn^{4+} emission is 5° C, of the green Mn^{2+} emission 260° C. With $CdWO_4$-U for the tungstate emission $T_1 = 45°$ C, for the uranate emission —70° C, and with CdI_2 $T_1 < -180°$ C for the CdI_2 emission, $T_1 = -80°$ for the lead emission, and +110° C for the manganese emission. Obviously the quenching

temperature is determined neither by the activator only, nor by the matrix lattice only, but by the combination of the activator and the surrounding lattice. As far as the matrix lattice is concerned, the crystal structure has a great influence: α and β $MgWO_4$ behave differently. Yet other properties of the lattice are also of importance. In series of compounds having identical structures, the temperature dependence of corresponding emissions varies systematically, in parallel with the chemical changes. In the series formed by *Ca*-, *Sr*- and *Ba*-compounds for instance, the *Sr*-compounds occupy an intermediate position in all cases (Table XXV) [1]. The quenching

TABLE XXV

Luminophor	T_2			Crystal structure
	Ca	*Sr*	*Ba*	
		←		
XWO_4	135	5	<—180	Scheelite
$XMoO_4$	75	—80	<—180	,,
$XSnO_3$-Ti	20	—40	<—40	Perowskite
X_2SnO_4-Ti	200	180	40	X_2SnO_4
		→		
$XO.6Al_2O_3$-Mn	460	540	600	β-Al_2O_3

temperatures further depend on the perfection of the crystals, badly crystallized products having a low quenching point. In some cases incorporation of foreign ions has a similar effect.

A point of particular interest is the influence of the exciting intensity on the quenching range observed with ZnS and Zn_2SiO_4-Mn.

Turning to the quenching range we find that in the majority of cases the quenching is completed within a comparatively narrow temperature interval (ΔT) varying from 70° to 200° C. When wider quenching ranges occur, we are justified

[1] P. LENARD–V. KLATT, *Ann. Phys.*, **15** (1904) 452, observed that the quenching temperature of *BaS* phosphors was much lower than that of the corresponding *CaS* and *SrS* phosphors.

in looking for some complication. Thus with *$MgSnO_3$–Ti*, *Zn_2SiO_4–Mn*, *$(Zn–Be)_2SiO_4$–Mn*, *$CaWO_4$–$PbWO_4$*, *$SrWO_4$–$PbWO_4$* and *$BaWO_4$–$PbWO_4$*, the wide quenching range is caused by the complexity of the emission spectra which consist of a number of superposed bands, each depending on the temperature in a different way. The same probably applies to cerium luminophors.

For the faintly luminescent *Mg_2TiO_4–Mn* (Chapter II, Section 2) an explanation is suggested by the blurred emission spectrum, especially remarkable by comparison with the sharp spectrum of the optimally fluorescing annealed products. Each activator atom is probably placed in slightly different surroundings, and accordingly the luminescence originating in each of them is quenched at a slightly different temperature. The same explanation probably applies to glasses.

For the interpretation of the temperature effects we have to distinguish between the different ways in which the luminescence has been excited. Therefore in Table XXIV the mechanism of excitation has been indicated. Excitation in an absorption band corresponding to the emission has been indicated by A, excitation in an absorption band connected with the activator, but not corresponding to the emission [1], by B, while excitation in an absorption band of the matrix lattice has been indicated by C.

The first kind of excitation is the simplest. Systems in which pure excitation of this kind occurs, invariably show a temperature dependence of fluorescence of type 1 (Fig. 68). Excitations of the two other kinds, leading to higher excited states, may also cause emissions which depend on the temperature in the same way. Here, however, the other types may also occur — and frequently do so.

In a number of cases the fluorescence increases with the temperature (Fig. 68, curve 3). In some of these cases the increase in the band under consideration is accompanied by a decrease in another band, e.g. in: *$CaWO_4$–Sm* (Chapter III,

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[1] An example of this kind of absorption is the *Mn_2SiO_4* absorption in *Zn_2SiO_4–Mn_2SiO_4*, observed between 2200—3000 Å.

Section 8), *ZnS–Zn–Cu* (this Chapter, Sec. 2.2), CdI_2–$MnCl_2$ (Fig. 58), *TlCl–Mn* and *CuCl*[1], *CaS–Cu–Ni*[2].

In other systems, however, no other band can be detected: e.g. in *CaO* (Sec. 2.10), $SrSiO_3$–*Ti*, $MgSiO_3$–*Ti*, Li_4SiO_4–*Ti* (Fig. 50), $CdSiO_3$–*Mn* (Sec. 2.4), $Cd_2B_2O_5$–*Mn* (Sec. 2.3) and some samples of *ZnS–Zn(NaCl)* and *ZnS–Ag(NaCl)* (Fig. 52). In such systems dissipation of the excitation energy is predominant both at low and at high temperatures, fluorescence occurring only in an intermediate region.

In the following sections we shall give a survey of the theories developed to explain the temperature effects mentioned above.

3. THEORETICAL

3.1 Temperature quenching in directly excited centres

When a centre has been excited by absorption in a band corresponding to its emission, the system may return to the ground state in two ways: either with the emission of radiation (fluorescence), or without radiation (dissipation).

If the probability of the first process is K_{lum}, that of the dissipation process K_{diss}, the efficiency η of the fluorescence process is given by the expression

$$\eta = \frac{K_{lum}}{K_{lum} + K_{diss}} = \frac{1}{1 + \dfrac{K_{diss}}{K_{lum}}}. \qquad (1)$$

Since there is no reason why K_{lum} should be very much dependent on the temperature, K_{diss} must be mainly responsible for the temperature dependence of the efficiency such as has been observed:

$$K_{diss} = f\,(T). \qquad (2)$$

Expression 1 gives a curve of type 1 (Fig. 68) if K_{diss} increases with the temperature.

For the dissipation process several theories have been proposed. A first group of theories is based on the fact that for pure crystals as well as for activated crystals there is

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[1] J. T. Randall, *Trans. Far. Soc.*, **35** (1939) 9.
[2] P. Lenard–F. Schmidt–R. Tomaschek, *Handb. Exp. Phys.*, Leipzig **23** (II) 749.

nearly always a fairly sharp long wave-length limit to the absorption; the emission occurring after excitation is situated either close to the edge of the absorption to which it corresponds, or is slightly displaced towards longer wave-lengths, but lies at least always below a certain wave-length: the long wave-length limit of the emission. As a consequence there seem to exist no electronic levels between the excited state and the ground state. If this is the case, a gradual loss of excitation energy is impossible. Whenever dissipation of excitation energy occurs, the excitation quantum must be transformed into vibrational energy in one process. The mechanism of such processes will be discussed in Section 3.2.

On the other hand there are several systems in which the situation described above does not exist. In some of them the occurrence of absorption bands at the long-wave side of the excitation region offers direct proof of the existence of intermediate excited states. In others the presence of such states is only indirectly indicated. For such systems a second group of theories has been developed in which the rate of the dissipation process is determined by the transition from the normal excited state to this (inactive) intermediate excited state, the ultimate annihilation of the energy from the intermediate state being of no importance. These theories are considered in Section 3.3 and 3.4.

3.2 Direct transformation of excitation energy into vibrational energy

In the cases in which no intermediate levels exist, the quenching process must be determined by a direct transformation of electronic excitation energy into vibrational energy. Since a vibration quantum is only a comparatively small unit, on the average not much larger than $^1/_{50}$–$^1/_{100}$ of the energy to be disposed of, our problem consists of the seeking of a model for the transformation of an electronic excitation quantum into a large number ($g = 50$–100) of vibrational quanta. The vibrations which are excited in this process may either involve the whole crystal, or only the centre of luminescence and its nearest neighbours.

When the entire crystal is involved, a satisfactory description of the energy transfer might be given by a picture in which the energy of the excitation quantum is distributed in one single process as a number of g phonons over the normal lattice vibrations. For pure lattices this problem has been treated theoretically by PEIERLS [1], FRENKEL [2], and MÖGLICH and ROMPE [3].

It is evident, however, that this description is not sufficiently detailed to account for the rather obvious fact that immediately after the electron jump downwards, the atoms in the neighbourhood of the jumping electron have a greater probability to obtain an abnormally high vibrational energy than the atoms which are situated at greater distances. Therefore a treatment based on the assumption that primarily only the nearest neighbours are involved in the transformation of energy seems more appropriate: immediately after the electron jump most of the excitation energy is localized as kinetic and mutual potential energy on the atoms in the immediate neighbourhood of the excited spot. Afterwards this localized vibrational energy is gradually spread over the whole crystal by interaction with the farther surroundings. A process of this kind [4] has been considered by MOTT [5] and SEITZ [6].

In the following we shall give a short survey of the theories

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[1] R. PEIERLS, *Ann. Phys.*, **13** (1932) 905.

[2] J. FRENKEL, *Phys. Z. Sowjet Union*, **9** (1936) 158.
Cf. also *Phys. Rev.*, **37** (1931) 17, 1276.

[3] F. MÖGLICH–R. ROMPE, *Z. Phys.*, **115** (1940) 707; **117** (1940) 119; *Naturw.*, **29** (1941) 109, 129; *Phys. Z.*, **41** (1940) 236.

[4] The authors do not pay much attention to the question as to which atoms in the crystal must be taken into account. Strictly and formally their consideration could be applied to a few atoms as well as to a crystal as a whole. Physically, however, the model is only acceptable when the vibration is more or less localized, i.e., when only a fraction of the crystal is involved in the process — and this is exactly what is needed for our purpose.

[5] N. F. MOTT, *Proc. Roy. Soc. London* (A), **167** (1938) 384.
R. W. GURNEY–N. F. MOTT, *Trans. Far. Soc.*, **35** (1939) 69.
N. F. MOTT–R. W. GURNEY, *Electronic processes in ionic crystals*, Oxford 1940, p. 218.

[6] F. SEITZ, *Trans. Far. Soc.*, **35** (1939) 74; *The modern theory of solids*, New York – London 1940, p. 450.

proposed by the various authors, together with a consideration of the consequences of these theories for the quenching of luminescence.

3.2.1 *The theories of* PEIERLS, FRENKEL *and* MÖGLICH *and* ROMPE

PEIERLS discussed the probability of transitions between the states of a lattice in which

a. all electrons are in the ground state and the crystal vibrates with N quanta in its normal vibrations;

b. one electron is excited, whereas the crystal vibrates with $(N-g)$ quanta.

This probability depends on the coupling between the electronic states and the vibrational states. Quantum-mechanically the coupling is given by an integral including the wave functions of normal and excited states and a perturbation term.

According to PEIERLS two kinds of solids can be distinguished: those for which the perturbation term is small and those for which it is so large that the perturbation method no longer holds. Though in the last case an exact calculation is not possible, PEIERLS believes that in solids of this group the dissipation of energy usually predominates over the emission process at all temperatures: they are pure "*absorbers*".

In the case of a small perturbation term, PEIERLS states that the probability of the dissipation is extremely small compared with that of a radiation process, and he gives several arguments in support of this point of view. In this case the solids are called "*scatterers*". With increasing temperature the probability of dissipation increases, but before it is comparable with that of the radiation process, the perturbation term has already grown so large that further calculation is impossible. This means that solids can exist which are scatterers at low temperatures, but absorbers at high temperatures. This is analogous to the phenomena of quenching of fluorescence, but it must be emphasized that according to PEIERLS a detailed calculation of the effect is impossible. Moreover it is doubtful, whether this picture may be applied at all to

the quenching mechanism of luminescence. In the case of fluorescence there may be a large difference between the wave numbers of the absorbed and emitted light, which is usually ascribed to a rearrangement of the atoms of the lattice in new equilibrium positions after the light quantum is absorbed. In PEIERLS' theory of the scattering process, however, it is essential that the energy connected with these rearrangements does not exceed the zeropoint energy of the lattice vibrations. In the work of FRENKEL, who has treated the problem along slightly different lines, this difficulty has been overcome and the possibility of new equilibrium positions, differing considerably from the original positions, is taken into account. In this way of approach the difficulties of an exact calculation of the probability of transitions without radiation are, however, also too great.

MÖGLICH and ROMPE, neglecting PEIERLS' arguments which forbid the application of the calculation method for large perturbations, have ventured to apply it over the whole range and were thus able to express the probability of the dissipation process in a form which contains the temperature explicitly, viz.

$$K_{diss} \sim f(g)\, T^g. \tag{3}$$

Disregarding the fundamental objections which may be made against the last treatment, these theories in their original form may be applied to the dissipation processes in pure lattices and perhaps to the dissipation of the excitation energy of a constituent ion of the base lattice in activated products, but certainly not to the interaction of a foreign ion with the lattice in which it is incorporated. Experiments on the quenching of luminescence, however, indicate that in a great majority, of cases the quenching is not a property of the lattice as such but of the emission centres and their surroundings. Therefore our primary need is for a theory which deals with the problem of dissipation from a centre. Possibly the theories might be modified to fit these cases, leading to an expression which contains the temperature in the same way as (3).

Substituting (3) into expression (1) of Section 3.1 gives

an expression for the temperature dependence of the efficiency which roughly corresponds with that found experimentally. The efficiency remains nearly unity from low temperatures up to a certain temperature, above which it drops rather sharply. The quenching range predicted by MÖGLICH and ROMPE's expression is not unsatisfactory either: at 50° K, for instance, it leads to a quenching range $\Delta T = 50°$ for $g = 50$, and half this value for $g = 100$.

In this theory the influence of lattice flaws and perturbations in general can be accounted for by assuming that such influences increase the probability of the dissipation reaction. It can, however, not be modified to such an extent that it can explain the phenomenon of energy transfer as observed with ZnS phosphors (Sec. 2.2) and tungstates and molybdates activated by samarium (Chapter III, Sec. 8). In spite of the rather satisfactory numerical agreement shown above, this theory therefore has to be discarded as a theory for the quenching of luminescence. Yet the mechanism may play a role in the dissipation of smaller quanta, as is necessary, for instance, when a big quantum is transformed into a smaller one with the dissipation of the energy difference.

3.2.2 *The theories of* MOTT *and* SEITZ

According to MOTT and SEITZ a crystal, or rather a centre and its surroundings, may be treated as a single vibrator, in the same way as is usual for diatomic molecules [1]. Its energy may be given as a function of the displacements of its constituent atoms or ions. As the displacements from the equilibrium positions are rather complicated in this case, the model must be greatly simplified. Instead of giving a complete description in terms of the true displacements along the real coordinates, which would require three times as many coordinates as there are atoms involved in the change, MOTT describes the situation schematically as a function of one

[1] This way of treating the problem is exactly the same as that of TELLER for internal quenching of large organic molecules (E. TELLER, *J. Phys. Chem.*, **41** (1937) 109).

generalized coordinate, a parameter defining the positions of all atoms at once.

Fig. 69*a* shows the energy of the normal and excited electronic states as a function of the configurational parameter. As the stable configuration of the constituents of the lattice in the neighbourhood of the excited centre will be different
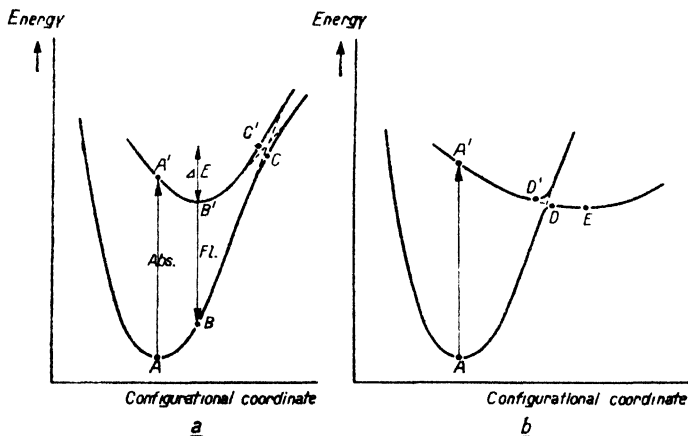
Fig. 69. Potential energy curves for the ground state and the excited state:
a. for a luminophor (MOTT, SEITZ).
b. for a pure absorber (SEITZ).

for both states, the minima of the two curves do not correspond. Normal optical transitions between the ground state and the excited state are restricted by the FRANCK–CONDON principle and occur without changing the atomic configuration (vertical jumps in Fig. 69). Adaptation of the position of the surrounding atoms to the changed situation occurs only after the electronic transition has taken place. The system moves downwards in the mould of the curve and the excess energy is dissipated as heat.

From this state the system may return to the ground state in two ways. In the first place the system may change from the excited to the normal electronic state. In this process the energy difference between the two states is emitted as

radiation (fluorescence). In the second place the transition from the electronic excited state to the normal state may occur without radiation. Transitions of the latter kind require identical atomic positions as well as equal energy and accordingly occur only when both the energy and the configuration of the atoms in a certain n^{th} vibration state of the excited state happens to correspond to a different, $(n+g)^{th}$ vibration state of the ground state. In Fig. 69 these states are denoted by C and C'; at these points the potential energy curves approach each other closely. Once the transition from the upper curve to the lower curve has taken place, resulting in a strongly vibrating centre, the localized vibrator may gradually lose energy, bringing the more distant surroundings to vibration. The system moves down along the lower curve and the liberated energy is distributed in the form of thermal waves over the whole crystal. In order to see where the temperature may play a part, we shall discuss the three stages of the dissipation process separately:

1. the move from B' to C';
2. transition from the excited state C' to the "ground state" C.
3. distribution of the vibrational energy (move from C to A);

re 1. The chance to move a system from the stable state at B' to the vibration state C' is approximately given by a BOLTZMANN factor

$$\nu e^{-\Delta E/kT} \tag{4}$$

n which ΔE is the energy difference between B' and C' and ν is the frequency of the vibration.

re 2. The transition between the curves from C' to C takes place nearly without change of energy and accordingly the probablity will be nearly independent of the temperature. It depends on the coupling which exists between the electronic state and the vibrations; it is small when this coupling is small. This is probably realized in excited systems which are well screened off from the surroundings, e.g. in the rare earths.

re 3. The disintegration of the vibration "packet" depends on the interaction of the localized vibrator with the surrounding

vibrators and will certainly be dependent on the temperature.

It is usually assumed that the first step determines the velocity of the dissipation process. If this is accepted, this velocity is given by the expression

$$K_{diss} = A\nu e^{-\Delta E/kT} \tag{5}$$

in which A is the probability of the transition between the curves from C′ to C.[1]

The influence of the nature of the ions which form the vibrating configuration is found in ν and ΔE. When m is the reduced mass of the ions participating in the (harmonic) oscillation and f is the restoring force, the frequency ν of the oscillation is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}}. \tag{6}$$

An influence of the polarizability of the ions as suggested by WEYL[2] may operate through a change in the shape of the potential curve, by which both the force constant f — and therefore ν — and the energy barrier ΔE are varied.

An influence of a variation of masses as indicated by (6) is very difficult to prove: since the dissipation varies with $\sqrt{m}$, but varies exponentially with ΔE, a slight variation in ΔE accompanying the replacement of an ion by another one may easily overshadow the variations of m. This may be the reason that in some series of compounds of calcium, strontium, and barium having the same structures (Section 2.12, Table XXV) the quenching increases from *Ca* to *Ba*, which is just the opposite of what would be expected from expression (6).

Expression (5) clearly indicates that the dissipation increases with increasing temperature. Inserting this expression in (1), we obtain for the temperature dependence of the efficiency of the luminescence

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[1] F. E. WILLIAMS–H. EYRING, *J. Chem. Phys.*, **15** (1947) 289, propose a similar formula, different only in that it contains an additional factor T. The influence of the extra factor is, however, negligible with respect to that of the exponential.

[2] W. A. WEYL, *Ind. Eng. Chem.*, **34** (1943) 1035.

$$\eta = \left(1 + \frac{A\nu}{K_{lum}} e^{-\Delta E/kT}\right)^{-1}. \tag{7}$$

This expression gives a constant efficiency near unity at low temperatures and a gradual, rather steep decrease above a certain higher temperature, in good agreement with what is found experimentally. The quenching range was defined in the experimental part (Section 2.12) as:

$$\Delta T = T_2 - T_1 = \frac{100}{80\text{–}20}(T_{0.2} - T_{0.8})$$

where $T_{0.2}$ and $T_{0.8}$ are the temperatures at which the efficiency is respectively 0.2 and 0.8 of the maximum value.

From (7) we obtain for ΔT:

$$\Delta T = \frac{10}{6} \cdot \frac{\Delta E}{k}\left(\frac{1}{\ln \frac{A\nu}{K_{lum}} - \ln 4} - \frac{1}{\ln \frac{A\nu}{K_{lum}} + \ln 4}\right) \tag{8}$$

and for the upper limit of the quenching range

$$T_2 = T_{0.2} + \frac{1}{5}\Delta T = \frac{\Delta E}{k}\left\{\frac{4}{3\left(\ln \frac{A\nu}{K_{lum}} - \ln 4\right)} - \frac{1}{3\left(\ln \frac{A\nu}{K_{lum}} + \ln 4\right)}\right\} \tag{9}$$

Thus the quenching range as well as the point of complete quenching are both determined by $\Delta E/k$ and $A\nu/K_{lum}$.

By dividing expression (8) by expression (9) we obtain an expression for $\Delta T/T$ showing that this quotient depends on $A\nu\ K_{lum}$ only:

$$\frac{\Delta T}{T} = \frac{6 \ln 4}{3 \ln \frac{A\nu}{K_{lum}} + 5 \ln 4}. \tag{10}$$

Since it is known that K_{lum} varies between rather wide limits, $A\nu/K_{lum}$ is probably also different for different systems. Therefore there is no reason why there should be a simple relation between ΔT and T. In fact the experimental data assembled in Table XXIV and represented graphically in Fig. 70 do not seem to indicate such a simple relationship.

An additional reason for the wide variations in the value
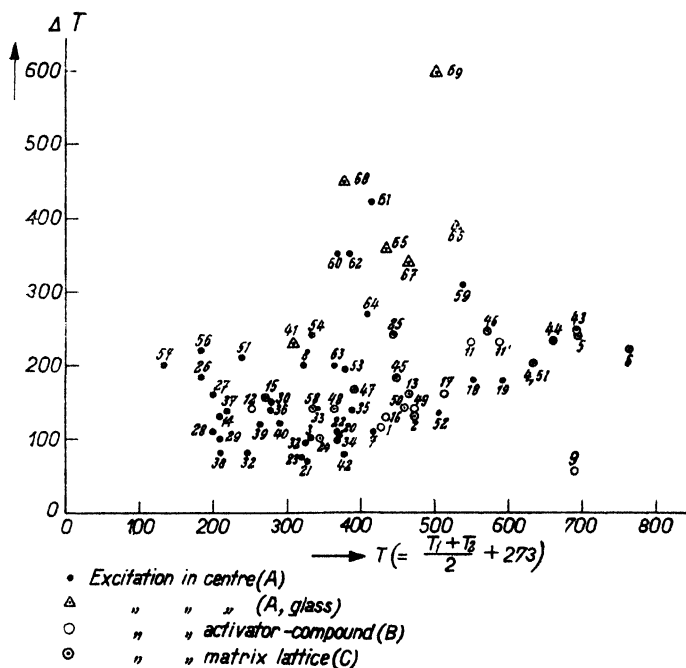
Fig. 70. The relation between the quenching range and the quenching temperature according to the data from Table XXIV. The numbers refer to this table.

of $\Delta T/T$ is the probable variability of ΔE. So far we have assumed that ΔE is constant. If it is a function of the temperature [1], e.g.

$$\Delta E = \Delta E_0 + aT$$

the expression (5) changes into

$$\nu\beta e^{-\Delta E/kT}, \text{ with } \beta = e^{-a/k} \qquad (5_1)$$

Then $\Delta T/T$ is dependent on $A\nu\beta/K_{lum}$ and contains the additional factor β which will probably also vary from case to case.

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[1] This is generally the case in processes which are regulated by a Boltzmann factor, such as diffusion, conductivity, etc.

In addition to these fundamental reasons for the variations of the values found for $\Delta T/T$, these variations might be partly explained by the rather trivial effect that the quenching ranges observed are wider than might be expected for luminophors consisting of ideal crystals, the actual emission being a superposition of the emissions from centres with slightly different surroundings.

Quantitatively the formulae (7) and (9) do lead to acceptable results. If we assume that K_{lum} may vary from 10^2 to 10^8 sec.$^{-1}$, ν from 10^{11} to 10^{14} sec.$^{-1}$, and A from 1 to 10^{-3}, $A\nu/K_{lum}$ must have a value between 1 and 10^{12}. Substituting these limiting values in (10), we get

$$0.1 < \frac{\Delta T}{T_2} < 0.6$$

while equation (8) gives

$$6 \cdot 10^{-5}\, \Delta T < \Delta E < 1.4 \cdot 10^{-2}\, \Delta T \text{ eV}.$$

Or, for a quenching range $\Delta T = 100°$ as found experimentally, the theory leads to quenching temperatures T_2 between 170 and 1000° K and to activation energies between 0.006 and 2 eV. These values are in fair agreement with the experiment.[1] From this agreement it may be concluded reversely that the widths of the quenching ranges measured may have a real physical meaning and need not be due to a situation as suggested above, in which the quenching curve is a superposition of several quenching curves having the same shape, but a slightly different position on the temperature scale Such superposition effects will occur occasionally, however. and may be held responsible for exceptionally wide quenching ranges.

In addition to the model discussed above, SEITZ has proposed another model to explain the absence of luminescence in a number of solids. This model is also based upon the crossing of the potential energy curves, but differs from the model of

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[1] cf. also V. E. LASHKAREV–K. M. KOSSONOGOVA, *C.R. (Doklady) U.R.S.S.*, **54** (1946) 125.
F. E. WILLIAMS–H. EYRING, *J. Chem. Phys.*, **15** (1947) 289.

the luminescent systems in the mutual position of these energy curves and the way in which they cross: whereas in the picture for the luminescent systems the minimum of the upper potential curve B′ is located inside the lower curve (Fig. 69*a*), for the pure absorbers it is assumed that this minimum lies outside the curve of the normal state (*E*, Fig. 69*b*). In this way the electronic excitation energy may be transformed into vibrational energy without the necessity of crossing a potential barrier and hence might occur without the aid of heat motion.

A serious objection against this model has been brought forward by MOTT and GURNEY[1]: a rearrangement of atoms to the extent required by the model, is nearly always impossible because of the volume occupied by the ions. Only in particular cases, when extremely small atoms are involved, as for instance in the absorption by *KH* in *KCl* (*U* centres), this situation might occur.

Further, for some of the cases to which SEITZ wishes to apply this theory, the occurrence of luminescence has been proved (viz. the fundamental emissions of halides, *ZnS*, *CdS*, and *ZnO*; cf. p. 49 of this book). Therefore we believe that the assumed situation practically never occurs, all solids being able to show luminescence, provided the temperature be sufficiently low.

3.2.3 *Influence of lattice disturbances in the picture of* MOTT *and* SEITZ

In the picture of MOTT and SEITZ (Sec. 3.2.2) the quenching of excitation energy from a centre depends on the vibrational interaction of the centre with its environment. Therefore a variation of this environment will change the interaction — and thereby the quenching point. Although variations of the quenching point due to this cause might in principle occur in both directions, in practice only a decrease is found. The reason may be that the potential barrier determining the quenching is lower for asymmetric than for symmetric surroundings.

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[1] N. F. MOTT–R. W. GURNEY, *Electronic processes in ionic crystals*, Oxford 1940, p. 219.

The presence of centres with a low quenching point may affect the behaviour of the system as a whole in two ways. If no transfer of energy occurs between excited normal centres and perturbed centres, the luminescence will be a superposition of the emissions of centres of both kinds. As a consequence the total quenching curve, being built up of a number of similar curves having a slightly different position on the temperature scale, is a curve with a wide quenching range, the upper limit of which is nearly identical with that of a system containing only ideal centres. This situation seems to be realized in the faintly fluorescent Mg_2TiO_4–Mn^{4+}, in which both the chemical behaviour of the system and the blurred emission spectrum makes it probable that the tetravalent manganese ions which are responsible for the emission are placed near lattice flaws, each having a slightly different environment (cf. Chapter II, Section 2). When both perturbed and imperturbed centres are present in the lattice, it may also occur however that excitation energy absorbed in normal centres is transferred to disturbed centres.

Such a transfer will usually also require a transport of energy. It may take place in two different ways: either by electrons and holes moving separately, or by excitons (Chapter I, Sec. 3.2). In the first case the transport process may depend on the temperature; the consequences with regard to the temperature quenching will be considered in Section 3.4. The transport of energy by travelling excitons, however, is probably not dependent on the temperature. In this case the rate of the dissipation process is determined by the dissipation of energy from the disturbed centres. Now even a relatively small amount of perturbed groups may cause a considerable decrease of the quenching point.

Due to the necessity of moving excitons, this picture can only be applied to systems in which the particular excited state can occur all over the lattice, i.e. in systems in which the centre is a lattice constituent. Therefore this picture may be used to explain the low and wide quenching ranges of badly crystallized tungstates and molybdates (Chapter III, Sec. 4) and also the lowering of the quenching ranges

of the tungstate and molybdate emission in tungstates and molybdates containing samarium (Chapter III, Sec. 8). The consequences of this picture for the transfer of energy from tungstate or molybdate groups to samarium ions, resulting in a variation of the colour of fluorescence, will be discussed in the next section.

3.2.4 *Transfer of excitation energy between different centres*

The picture developed in the preceding section also suggests an explanation of the phenomena of transfer of excitation energy between different centres in systems in which excitation does not give rise to free electrons.

Let us for instance consider a tungstate containing samarium
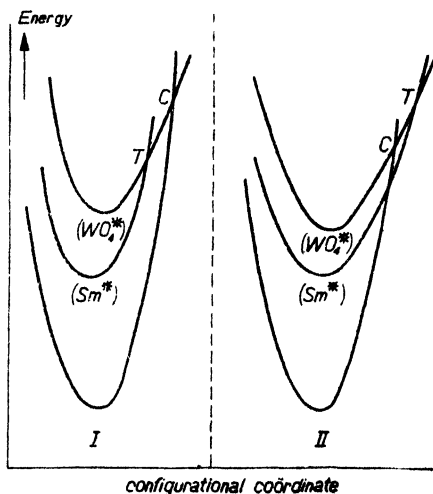
Fig. 71. Two possible potential energy curves for different excited states of a tungstate activated by samarium.

n which an exciton, primarily formed in a normal tungstate group, has finally arrived at a tungstate group next to a samarium ion. Starting from this situation two things may happen: the exciton may either be annihilated without radiation by the process discussed in the preceding section, or it

may be transferred to the samarium ion with dissipation of the energy difference. The proportion in which these two processes take place may depend on the temperature. In Fig. 71 we have drawn the energy curves for two possible situations. In Fig. 71^{I} it has been assumed that the transfer of excitation energy to the samarium ion involves a lower activation energy than the dissipation process. At low temperatures fluorescence occurs only in the tungstate band. Above the temperature at which the transfer of excitation energy to the samarium becomes possible, the tungstate fluorescence is completely or partly replaced by the samarium fluorescence. At a still higher temperature the dissipation process becomes predominant and the fluorescence is quenched [1]. The transfer of the exciton from the tungstate group to the samarium may however also require a temperature which is higher than the quenching temperature of the tungstate emission (Fig. 71^{II}). The tungstate fluorescence will then be found below a certain temperature, the samarium fluorescence above a certain higher temperature, but the system is non-fluorescent between these temperatures. This has actually been observed in certain cases (Chapter III, Section 8). Obviously intermediate situations are also possible. A limiting case, in which the samarium fluorescence increases just in the temperature range in which the tungstate fluorescence decreases, is realized in $CaWO_4$-*Sm*.

Transfer of energy between different centres as described here will only occur if the quantum of the first centre is larger than the quantum of the centre to which the exciton is transferred. Since the excited states reached in absorption are supposed to correspond directly to the emission, this means that transfer of this kind is always accompanied by an increase in the wave-length of the fluorescence. This does not imply, however, that the fluorescence of systems of this kind always changes to the long-wave direction with increasing temperature. If not one, but two or more different kinds of centres of the

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[1] This quenching occurs by dissipation from the excited tungstate group. In a complete discussion we have also to consider the quenching from the samarium ion. This however does not fall within the scope of this section.

samarium type are present, for instance one with a green, and the other with a red emission, it may well be that the transfer from WO_4^{2-} to the red centre has a lower activation energy than the transfer to the green centre. The fluorescence will then change from blue (WO_4) via red to green. It is obvious that also in this case both the red and the green fluorescence are at longer wavelengths than the tungstate fluorescence.

3.3 Quenching involving optically inactive excitons

The absence of a long-wave absorption does not necessarily imply the absence of an intermediate excited state. It may happen for instance that the probability of optical transition between the ground state and the intermediate state is small. In such cases the quenching process may be determined by the transition of the system from the normal excited state, reached in the optical excitation process, to the inactive intermediate state. In organic molecules tautomeric forms form such a state, and it has actually been shown that transformation of an excited molecule to these forms may play a part in the temperature quenching [1]. In solids such states would allow the storage of part of the excitation energy for a considerable time, while these states might also play a part in the transport of energy through the lattice. It was in fact in connection with such processes, viz. the migration of energy in various kinds of photo-chemical reactions, that FRANCK and TELLER [2] introduced such optically inactive excitons. These authors tried to give a theoretically well-founded picture of these excitons: while a normal optically active exciton would be a static, long-wave exciton, the inactive exciton would be a moving, short-wave exciton. The latter has a long life and is formed by a combination of a long-wave exciton with some phonons. We are not convinced, however, that the theoretical considerations upon which this picture is based are beyond doubt.

The picture involving intermediate states of this kind might

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[1] J. FRANCK–R. LIVINGSTONE, *J. Chem. Phys.*, **9** (1941) **184.**
[2] J. FRANCK–E. TELLER, *J. Chem. Phys.*, **6** (1938) **861.**

find use in the explanation of the temperature quenching in general, but it appears to be most attractive for those cases in which energy is transferred between different centres, as found with the tungstates and molybdates activated by samarium (Chapter III, Section 8). In such systems the tungstate or molybdate fluorescence would be quenched by the transition of the system from the normal excited state to the inactive intermediate state. If no centres of a different kind are present, the energy of the inactive state is finally dissipated as heat, for instance by the mechanism of MOTT discussed in Section 3.2.2. When samarium ions are present, the inactive excitons may traved to the samarium ions and hand over their energy to these ions, thus giving rise to the samarium fluorescence.

According to this picture the quenching of the tungstate or molybdate fluorescence is independent of the final dissipation of the inactive exciton: it must be the same whether this is an actual dissipation — as occurs when no samarium is present — or a transfer to samarium. But experiments show that the quenching point of tungstates and molybdates is lowered by samarium. Therefore even in these cases the picture does not account for the facts.

3.4 Quenching via intermediate states in systems with a bimolecular fluorescence process

For systems in which excitation gives rise to excitons, the picture of the quenching process involving intermediate excited states has been found to be unsatisfactory (Sec. 3.3). The situation is different, however, for systems in which excitation separates the excited electrons from their "holes", and in which the fluorescence process, determined by the recombination of electrons and holes, is bimolecular. For such systems the existence of intermediate states has not only been proved by absorption measurements, but there are also strong indications that these intermediate states are actually involved in the quenching process. The most important of these indications is the dependence of the quenching upon the intensity of excitation.

It has been shown in the experimental part (Section 2.2 of this Chapter) that the efficiency of the luminescence of *ZnS* in the quenching range depends on the intensity of the exciting radiation, high intensities of excitation giving rise to high efficiencies. From this it follows that the quenching range itself lies at higher temperatures for high than for low exciting intensities. This was actually directly measured (Fig. 55A). An explanation proposed by RIEHL [1] is based on the bimolecular character of the luminescence process in these systems. At high intensities of excitation the concentration of liberated electrons is large, and the time in which the electrons and holes recombine with the emission of fluorescence, being inversily proportional to the product of the concentrations of electrons and holes, is small. Therefore, according to RIEHL, the electrons are exposed to the chance of a transition without radiation only for a short time. This however is not correct if no further assumptions are made: the recombination without radiation nevertheless remains a recombination of electrons and holes and depends on the concentration of electrons and holes in the same way as the recombination accompanied by fluorescence. In order to explain the phenomena observed we have to assume that the rate of the quenching process is not determined by the bimolecular recombination process but by a process of lower order, probably a monomolecular one.[2] This process may be the transition of either the excited electrons or the electron holes to a certain intermediate state. A detailed model of such a process has been given by SCHÖN and KLASENS. It will be considered in the next section.

3.4.1 *The theory of* KLASENS–SCHÖN

In systems with a bimolecular fluorescence mechanism, particularly in zinc sulphide, a number of phenomena occur which can only be explained if we assume that energy transfer between centres of different kinds is possible. *ZnS* containing blue and green, or blue and orange centres shows a blue fluores-

[1] N. RIEHL, *Z. techn. Phys.*, **20** (1939) 152; *Phys. u. techn. Anw. d. Lumineszenz*, Berlin 1941, p. 117.

[2] F. URBACH–A. URBACH–M. SCHWARTZ, *J. Opt. Soc. Am.*, **37** (1947) 122, arrived at the same conclusion.

cence at high intensities of irradiation, but a green (or orange) fluorescence at low intensities [1]. Similar variations are caused by variation of the temperature (cf. Section 2.2).

The transfer of energy between different centres and the way in which it depends on temperature has been discussed by SCHÖN [2] and KLASENS [3].

In the orbital energy scheme normally accepted for *ZnS*, the matrix lattice gives rise to occupied and unoccupied energy bands, while activators (*Zn*, *Cu*) give rise to occupied localized levels situated between these bands, a little above the occupied one (Fig. 72). Excitation in the centres liberates electrons from the localized activator levels into the conduction band, electron holes remaining in the activator levels. Recombination of free electrons with the holes gives rise to fluorescence. During the time that the electrons are free, the holes may be filled up by electrons from the occupied lattice band, provided the energy necessary for this process is available. This will
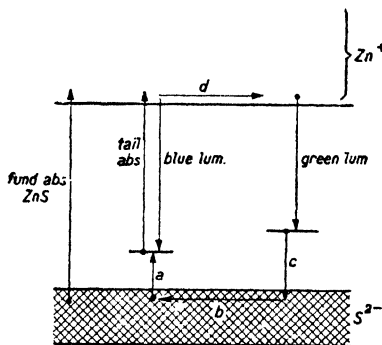
Fig. 72. The energy band scheme of a zinc sulphide luminophor The mechanism for the transfer of energy from the blue to the green centres according to KLASENS–SCHÖN is indicated by the arrows *a*, *b*, *c*, *d*.

[1] J. H. GISOLF–F. A. KRÖGER, *Physica*, **6** (1939) 1101.
[2] M. SCHÖN, *Z. Phys.*, **119** (1942) 463; *Forsch. u. Fortschritte*, **19** (1943) nr 23/24.
Cf. also K. BIRUS, *Ergebn. Exakt. Naturw.*, **20** (1942) 248.
[3] H. A. KLASENS, *Nature*, **158** (1946) 483.

be the case above a certain temperature which is connected with the energy gap ΔE by the relation

$$\Delta E \cong skT$$

in which s is a constant which is of the order of 15–20 [1]. Therefore at low temperatures holes once formed in a centre remain fixed, but at higher temperatures they may leave the centre. Once liberated, the holes may move through the lattice and, when meeting another centre, may be trapped. In this way a hole may migrate from a blue centre to another blue centre, but also to a green centre (*a–b–c*, Fig. 72).

The energy levels of blue and green centres are supposed to lie at different heights above the occupied band, the blue one a little closer to it than the green one. The temperatures at which holes may leave these centres are therefore different, and higher for green centres than for blue centres.

In consequence of the different energies of liberation for green and blue centres there is a tendency of the holes to migrate from the blue centres to the green centres.

Whether the effect discussed above takes place or not is determined by the rate of this process in relation to the rate of recombination. At low temperatures the migration of holes from blue to green centres is slow compared with the recombination of electrons and holes. At higher temperatures the migration of holes may become so rapid that nearly all holes migrate from blue to green centres before recombination occurs, resulting in a completely green fluorescence.

From this picture for the phenomenon of colour change of fluorescence, KLASENS has drawn the following conclusions:

1. the suppression of blue by green is equivalent to quenching.
2. for the suppression of the blue band the particular properties of the green centre are of no importance. The only essential point is that the green level is situated a little farther above the occupied band than the blue level; therefore
3. each disturbance giving rise to such an energy level will act as a quencher for the blue band.

[1] J. T. RANDALL–M. H. F. WILKINS, *Proc. Roy. Soc. London*, (A) **184** (1945) 390.

Such disturbances may consist of other activators, e.g. *Mn* in *ZnS–Zn*, but may also be ions which do not give rise to visible emission, e.g. *Fe, Ni, Co*. When no special quenchers like *Fe, Ni, Co* are present, the fluorescence is quenched by transfer of holes to similar levels, caused by lattice flaws, cracks, unoccupied ionic positions, or ions in the vicinity of the surface. Obviously similar considerations are valid for the quenching of the green fluorescence. In this case the quencher level must be situated a little farther above the occupied band than the green level.

In agreement with this theory the quenching range of a certain band is in fact shifted towards lower temperatures both by foreign quenchers and by lattice flaws. An example of the first influence is the effect of nickel on the quenching point of *ZnS–Zn* as reported by KLASENS (loc. cit.). The influence of lattice flaws is demonstrated by badly crystallized *ZnS–Zn* and *ZnS–Ag* which show luminescence in the common bands at low temperatures, but not at room temperature [1]. The same applies to crystals which have been distorted by unidirectional pressure, the well-known *"Druckzerstorung"*. The theory is further supported by the dependence of the quenching on the intensity of excitation, found for real quenching as well as for quenching by transfer of the excitation energy to another fluorescence centre, while it also accounts for quenching by infra red and specific killing of phosphorescence (Sec. 3.4.2). Therefore we are convinced that the basic idea underlying this theory is sound, although possibly the details still have to be changed to some extent. The mathematical formulation of the processes discussed above is comparatively simple if we make a few simplifying assumptions. We shall treat the general case that both blue and quencher centres are excited directly.

If a is the total number of ionizations of centres per unit time, a certain fraction r will occur in the blue centres, and a fraction $(1-r)$ in the quencher centres [2]. Let n be the number

[1] Bad crystallization may also cause a decrease of ΔE.

[2] r depends on the excitation conditions (wave-length of the exciting radiation.)

of free electrons per unit volume, b and k the number of holes in blue and quencher centres, a_b and a_k the probability coefficients of recombination of free electrons and holes in blue and quencher centres. For equilibrium conditions we then have

$$\frac{\mathrm{d}b}{\mathrm{d}t} = rq - a_b nb - cb = 0 \tag{1}$$

$$\frac{\mathrm{d}k}{\mathrm{d}t} = (1 - r)\, q - a_k nk + cb = 0 \tag{2}$$

in which c is the velocity with which a hole moves from a blue to a quencher centre. c depends on the relative number of blue and quencher centres B and K. If we assume that holes, once captured in a quencher centre cannot return to a blue centre, c varies exponentially with the temperature with an exponent $\Delta E/kT$ in which ΔE is the energy difference between the blue level and the occupied band. If we further assume that the cross-sections for hole capture are the same for the different centres, c can be expressed as

$$c = s\frac{K}{K + B}\, e^{-\Delta E/kT} \tag{3}$$

in which s is a constant.

These equations lead to an expression for the ratio between the recombination taking place in the blue and in the quencher centres, i.e. between the intensity of the blue fluorescence I_b and the "intensity" of the quenching I_k:

$$\frac{I_b}{I_k} = \frac{r}{(1 - r) + \dfrac{c}{\sqrt{aq}}} \tag{4}$$

if $a_b = a_k = a$, while the efficiency of the blue band (η_b) is given by

$$\eta_b = \frac{I_b}{I_b + I_k} = \frac{r}{1 + \dfrac{c}{\sqrt{aq}}} \tag{5}$$ [1]

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[1] For exclusive excitation in the blue centres ($r = 1$) this expression is identical with expression (1) given in Section 3.1. As is easily seen by adding (1) and (2), $n^2 = q/a$, and therefore:

$$\frac{K_{diss}}{K_{lum}} = \frac{cb}{anb} = \frac{c}{\sqrt{aq}}.$$

If c is small, the efficiency of the blue luminescence is only determined by the relative strength of the absorption of the centres. When c increases, which happens with increasing temperature, the quenching process increases at the cost of the blue fluorescence process, so that finally the blue emission is completely suppressed.

The influence of the intensity of excitation is also accounted for. For a certain excitation, i.e. a certain q,

$$\frac{c}{\sqrt{aq}} \cong \frac{e^{-\Delta E/kT}}{\sqrt{aq}}$$

will become important above a certain critical temperaturel For a larger value of q (stronger excitation) the same critica value of $c/\sqrt{aq}$ is reached at a higher temperature, which means that the quenching curve is shifted towards higher temperatures. Quantitatively the agreement with experiment is not quite satisfactory: the formula gives a dependence of the efficiency of luminescence on the square root of the exciting intensity, while both URBACH [2] and GARLICK [2] observed a dependence on the first power, and some times even higher. In recent papers KLASENS c.s. [3] have pointed out that the first power can be accounted for if it is assumed that the cross-section of the quencher centres is much larger than that of the blue centres ($a_k \gg a_b$).

3.4.2 *Specific occurrence and suppression of phosphorescence*

If a zinc sulphide luminophor contains blue centres together with green copper centres, or blue centres together with orange manganese centres, fluorescence occurs in the bands of both centres, but phosphorescence only occurs in the bands of the green or orange centres. This has been explained by assuming that the traps involved in the phosphorescence process are formed by the copper and the manganese, thus causing an increased chance of recombination of electrons

[1] F. URBACH–A. URBACH–M. SCHWARTZ, *J. Opt. Soc. Am.*, **37** (1947) 122.

[2] G. F. J. GARLICK–A. F. GIBSON, *Nature*, **158** (1946) 704.

[3] H. A. KLASENS–W. RAMSDEN–CHOW QUANTIE, *J. Opt. Soc. Am.*, **38** (1948).
H. A. KLASENS–M. E. WISE, *J. Opt. Soc., Am.*, **38** (1948).

released from traps with holes in these centres[1]. Although this assumption is quite reasonable, it is very difficult — if not impossible — to match it with phenomena like the specific quenching of phosphorescence by the killers *Fe, Co, Ni*[2], *Mn*[3], and *Ta*[4], which quench the phosphorescence while the fluorescence remains comparatively unaffected. On the other hand a satisfactory explanation of both killing and the specific emission of phosphorescence is accounted for in the theory of SCHÖN–KLASENS, if we assume that the electron traps do not belong to particular centres, but that electrons released from traps may recombine with holes in centres of different kinds all over the lattice.

Let us first consider a crystal containing blue and green centres, in which excitation has given rise to holes in the levels of the blue centres. If the electrons remain free, the time during which the holes may move from the blue to the green centres is determined by the recombination of electrons and holes. This time is long for low intensities of excitation. If the electrons are trapped however — and this is what happens in a phosphorescent system — the time during which the holes may migrate is increased. Accordingly the phosphorescence may be green while the fluorescence is still blue. It is obvious that these processes depend on the proportion between the rate of migration of the holes and the rate of recombination, rather than on the absolute values of these quantities. Since both the rate of the moving of the holes and of the release of trapped electrons vary with the temperature as $\Delta E_t/kT$, the relative magnitude of the trap-depths ΔE_t for holes and electrons will determine the behaviour of the

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[1] F. A. KRÖGER, *Dissertation*, Amsterdam 1940, p. 56, 114. G. F. J. GARLICK–A. F. GIBSON, *Nature*, **158** (1946) 704. J. H. GISOLF–F. A. KRÖGER, *Physica*, **6** (1939) 1101.
[2] E. WIEDEMANN–G. C. SCHMIDT, *Wied. Ann.*, **56** (1895) 201. R. COUSTAL–F. PRÉVET, *C.R. Paris*, **190** (1932) 1403. M. CURIE–J. SADDY, *C.R. Paris*, **194** (1932) 2040. J. SADDY, *C.R. Paris*, **209** (1939) 93. L. LEVY–D. W. WEST, *Trans. Far. Soc.*, **35** (1939) 128; *Brit. J. Radiol.*, **7** (1934) 344.
[3] J. EINIG, U.S.A. Pat. Spec. 2.220.894.
[4] M. C. G. DONCIEUX, D.R.P.A. S 143.123.

phosphorescence as a function of the temperature. The experiment shows that phosphorescence occurs in the blue band at low temperatures[1]. Therefore in this case ΔE seems to be larger for the holes than for the electrons, the holes being frozen in most effectively.

A similar reasoning applies to systems containing other activators. The phosphorescence generally occurs in the centres which are connected with levels which are farther above the lattice band than the levels of the other activator. This is the explanation of "specific" phosphorescence. This explanation, however, involves at the same time that the specificity has no general value, but is only valid for certain combinations of activators. Specific phosphorescence in the green copper band is for instance found in *ZnS–Zn–Cu* and *ZnS–Ag–Cu*, but in *ZnS–Mn–Cu* the phosphorescence is "specific" for the manganese!

When the system contains quencher centres instead of green centres, the mechanism remains the same, but in this case the phosphorescence occurs in the quenching centre, i.e. it is not observed at all. In the preceding sections we have seen that quenching of fluorescence is not only caused by transfer of energy to foreign ions as *Fe*, *Ni* etc., but lattice flaws and disturbed lattice points may also act as quenchers. This effect also finds its counterpart in the quenching of phosphorescence. When copper is incorporated in well crystallized zinc sulphide crystals, as are obtained by heating at a high temperature in presence of a flux, the system shows the strong, well-known green copper phosphorescence. If however copper is incorporated in badly crystallized products, e.g. crystals made at 700–800° C, the system shows a green fluorescence, but phosphorescence is not observed. In terms of the present theory this is explained by assuming that the first products contain only very few lattice flaws which may act as quenchers, while the latter products contain a large number of them.

In view of these facts we believe that the hypothesis of free recombination is preferable to that of restricted recom-

[1] F. A. Kröger, *loc. cit.*

bination. This does not imply, however, that the traps have nothing to do with the activators. There are strong indications that certain activators like copper and manganese increase the storage of energy much above the level occurring in systems which do not contain these activators, so that probably these activators cause traps.

Incidentally it may be emphasized here that with the acceptance of free recombination in phosphorescence, the theory proposed by GISOLF and KRÖGER[1] to explain the intensity dependence of the proportion between blue and green, or blue and orange emission bands loses its foundation. Specific phosphorescence is not the cause of this phenomenon, but both specific phosphorescence and the intensity dependence of fluorescence are a consequence of the same process: the migration of holes between different centres.

The theory of KLASENS–SCHÖN can also account for certain effects caused by infra red. Quenching for instance will occur if irradiation with the infra red increases the rate of the migration of a hole to a quencher by liberating it from its original centre. In systems in which fluorescent centres of other kinds are present, irradiation by infra red causes glow in the bands of the other activator instead of quenching[2].

When entering more deeply into the details of the process, in some cases phenomena are met which are not explained by the theory in its simplest form. An example is the phenomenon observed by ANTONOV–ROMANOVSKII with *ZnS–Cu–Mn*[3]. This product shows phosphorescence exclusively in the manganese band, the green phosphorescence being killed by a mechanism such as discussed above. Irradiation with infra red long after the interruption of the excitation causes only an orange glow. The same irradiation applied immediately after the interruption, however, causes also a glow in the green band. This seems to prove that in the first moments the holes are still in the green centres. But in that

[1] J. H. GISOLF–F. A. KRÖGER, *Physica*, **6** (1939) 1101.
[2] P. BRAUER, *Z. Naturforsch.*, **1** (1946) 70; Chapter I, Section 10.
[3] V. V. ANTONOV–ROMANOVSKII, *Bull. acad. sci. U.R.S.S.*, sér. phys., **9** (1945) 364.

case it cannot be explained why the phosphorescence at this same moment is not green, but orange.

This behaviour can however be explained if it is assumed that the cross-section for recombination of electrons with holes is larger for manganese centres than for copper centres, an assumption which is identical with the one made by KLASENS to obtain quantitative agreement for the intensity dependence [1].

3.4.3 *Increase of fluorescence with the temperature*

So far the transfer of excitation energy between different centres has been considered mainly from the point of view of the centres which lose their excitation. Obviously similar considerations apply to the centres to which the energy is transferred. Next to expression (5) of Section 3.4.1 giving the decrease of the blue emission we have for instance the following expression for the efficiency of the fluorescence in the centres of the other kind, e.g. green centres:

$$\eta_g = \frac{I_g}{I_b + I_g} = \frac{(1 - \varkappa') + \dfrac{c'}{\sqrt{aq}}}{1 + \dfrac{c'}{\sqrt{aq}}} \tag{6}$$

which gives the increase of the green process in the same temperature range in which the blue process decreases. This green luminescence may be replaced by still another one, or it may be quenched.

Since the quenching centres are completely comparable with the fluorescence centres, it may also happen that a certain fluorescence, e.g. the blue one, is quenched by transfer of excitation energy to a quencher centre with an occupied level situated a little farther above the occupied band of the matrix lattice. But the quencher in its turn may lose the excitation energy by transfer of the excitation energy to a fluorescence centre with an occupied level lying still a little higher: the quenching is quenched! In this way it may happen that a system showing a blue fluorescence at low

[2] Cf. our remarks at the end of Section 3.4.1.

temperatures, is non-luminescent at an intermediate temperature and shows green fluorescence at a higher temperature (obviously followed by final quenching at a still higher temperature). This is realized in the system *ZnS–Zn–Co–Cu* [1].

When the first emission takes place only at an extremely low temperature — or when it does not occur at all, the energy being primarily absorbed in the quencher — we have a system which is non-fluorescent at low temperatures, but which becomes fluorescent at higher temperatures [2]. This phenomenon has been observed with some samples of *ZnS–Zn* (*NaCl*) and *ZnS–Ag* (*NaCl*) (Sec. 2.2, Fig. 52).

So far we have only met a variation of the colour of fluorescence with the temperature in such a way that an increase of the temperature favours the emission of the longer wavelengths. This is a consequence of the theory, if the intermediate levels which play a part in the transfer mechanism are directly involved in the fluorescence process, i.e. if the wave-length emitted in fluorescence is determined by the energy difference between the hole traps and the conduction band. This condition, however, need not to be fulfilled. For manganese for instance we know that emission occurs in characteristic bands of the divalent manganese ion. In the orbital energy scheme the Mn^{2+} levels are probably situated much lower than the levels involved in the transfer process (cf. Chapter I). This situation has been drawn in Fig. 73. Holes which have migrated to the *Mn*(*Cl*) level are filled by electrons from the conduction band. Energy liberated in this process is used to excite manganese to one of its characteristic excited states, which is finally followed by the characteristic manganese fluorescence when the manganese ion returns to the ground state. For *Ni*, *Fe* and *Co* the situation is probably similar [3].

In the presence of such centres the rule of increasing wavelength does not hold: blue may be replaced by violet, red by green, etc. Actually LENARD mentions several cases in which

[1] H. A. KLASENS, private communication.

[2] The explanation given here has been indicated by Dr KLASENS in a private communication.

[3] *ZnS–Fe* shows fluorescence in the infra red A. A. BUNDEL a.o., *Bull. acad. sci. U.R.S.S.*, sér. phys., **9** (1945) 543.
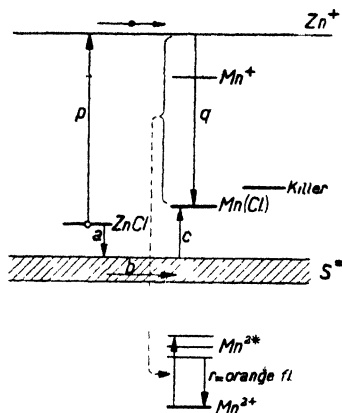
Fig. 73. Orbital energy scheme for *ZnS–Zn–Mn* (*NaCl*) containing a killer.

a colour change of this kind occurs, e.g. *CaS–Cu–Ni* [1] in which the fluorescence changes from red at low temperatures to green at higher temperatures.

3.5 Colour change of fluorescence in the model of Mott–Seitz and of Klasens–Schön

In a number of systems in which centres of different kinds are present, the emitted fluorescence varies with the temperature, one band being predominantly emitted at low temperatures, the other at higher ones. This has been observed with $CaWO_4$–*Sm* (Chapter III, Sec. 8), *ZnS–Zn–Cu* etc. (cf. preceding sections). It has also been found that the fluorescence in a certain band is quenched, while fluorescence in another band appears at a much higher temperature.

Although the phenomena are perfectly similar, different explanations have been proposed for systems in which excitation gives rise to excitons — and in which also the transport of energy is supposed to take place by means of excitons — (Sec. 3.2.4), and in those in which electrons are separated

[1] P. Lenard–F. Schmidt–R. Tomaschek, *Handb. Exp. Phys.*, Leipzig **1928**, **23** (II) **749**.

from their holes (Sec. 3.4.1). The essential difference between the two proposed mechanisms is that in the first mechanism the activation energy causing the temperature dependence of the phenomena has been sought in the potential energy of the ions while in the mechanism proposed by SCHÖN–KLASENS it is energy of the electronic configuration. As far as we see this difference is not a necessary consequence of the different ways of energy transport. Therefore further experiments are required to show whether the acceptance of such fundamentally different mechanisms is justified or not.

3.6 Variation of the exciting absorption

We cannot close the discussion of the variations of fluorescence with the temperature without having mentioned another mechanism by which the fluorescence of a system may vary with the temperature.

Let us consider as an example *ZnS–Cu*, containing electron traps. Upon excitation in the copper centres electrons are brought to the conduction band, the holes remaining in the copper centre. When part of the excited electrons is trapped, a corresponding number of copper levels remains unoccupied. Accordingly the absorption in the absorption band of the copper centre is diminished. When the temperature is increased the trapped electrons are liberated so that the holes in the copper can be filled and the copper centres may become active in absorption again. In this case an increase of fluorescence in a certain band is observed at the temperature at which thermal glow occurs in thermo-luminescence [1]. This has been observed with *ZnS–Cu* and *ZnS–Mn* (Sec. 2.2). Decrease of absorption during excitation has actually been found for these systems, and also for *CaS–Bi* [2].

3.7 Excitation in absorption bands not corresponding to the emission

In the preceding sections we have started studying the

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[1] G. F. J. GARLICK–M. H. F. WILKINS, *Proc. Roy. Soc. London*, **A 184** (1945) 427.

[2] P. LENARD–F. SCHMIDT–R. TOMASCHEK, *Handb. Exp. Phys.*, Leipzig 1928, **23** (I) 697.

behaviour of systems excited in bands corresponding to the emission. The phenomena of quenching by transfer of energy, however, have automatically introduced the situation which we wished to exclude at first: the fluorescence emitted by the centres to which energy has been transferred, is actually excited by energy primarily absorbed in the absorption band of the other centres.

This phenomenon occurs in a large number of cases, the most important of which is the excitation of the fluorescence of an activator by absorption in an absorption band of the matrix lattice. In such cases quenching may take place either by dissipation of energy from the high excited state before the energy has been transferred to the activator, or it may be quenched from the activator itself. It is obvious that the quenching point is determined by the dissipation process occurring at the lowest temperature. If the dissipation from the centre determines the quenching point, the same quenching point is found for direct excitation in the centre or for excitation to the higher state. If it is the annihilation of energy from the higher state, however, luminescence excited in the centre may show a higher quenching point. This seems to be realized in CdI_2–$MnCl_2$ (Sec. 2.5) and *ZnS–MnS* (Sec. 2.2). For *ZnS–Mn* it is possible to give a more detailed explanation. Let us consider the orbital energy scheme of this system (Fig. 73). Excitation with λ 3650 Å leads to a high excited state (transition q, reverse). From this state quenching may occur by migration of the hole from the *Mn*(*Cl*) levels to quencher levels. Characteristic excitation in the manganese ions, however, leads to the excited state of the manganese ions (transition r, reverse). From this state energy cannot be transferred to other states, the only possibility of quenching being the transformation of the excitation energy into vibrational energy which may occur by the mechanism discussed in Section 3.2.2.

Obviously the mechanism may be still more complicated if several excited states exist above the excited state from which the fluorescence starts. Dissipation processes may start from each of these states, and their relative importance will change with the temperature. Such effects must explain the

differences in behaviour between *ZnS–Mn* excited by λ 3650 Å in the *Mn*(*Cl*) absorption band and by $\lambda < 3300$ Å in the *ZnS* absorption band (Fig. 55).

3.8 Quenching by high activator concentrations

As a rule the efficiency of the luminescence as a function of the activator concentration increases at low concentrations but decreases again at higher concentrations, giving a maximum luminescence in an intermediate concentration region. This was formulated by BRUNINGHAUS in his law of the optimum ("loi d'optimum") [1]. According to this author, the decrease of the efficiency at higher concentrations is caused by absorption of the luminescence originating in one activator atom, by one of the other activator atoms. As the luminescence is nearly always shifted towards longer wave-lengths relative to the absorption, the emission and the absorption overlap only to a small extent. Accordingly only the short-wave part of the emission is absorbed, resulting in a changed spectral distribution of the emission. This phenomenon has actually been observed with cerium luminophors [2]. The decrease, however, usually occurs at concentrations at which the spectral distribution is not yet markedly changed and where the self-absorption must be rather small. Therefore, although self-absorption may account for a small decrease of the efficiency, it certainly does not do so for the strong effects. For these another explanation has to be found. An indication to a solution is offered by the observation that the decrease of luminescence at high activator concentrations is not found at low temperatures: the high concentration lowers the quenching temperature. This can be explained in several ways, dependent on the mechanism accepted for the temperature quenching.

In the frame-work of their own theory, MÖGLICH and ROMPE [3] suggest that the incorporation of activator atoms causes

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[1] L. BRÜNINGHAUS, *C.R. Paris*, **149** (1909) 1375.
Ann. chim. et phys., (8) **20** (1910) 519; **21** (1910) 210.
[2] F. A. KRÖGER–J. BAKKER, *Physica*, **8** (1941) 628.
[3] K. BIRUS–F. MÖGLICH–R. ROMPE, *Phys. Z.*, **44** (1943) 122.
M. SCHÖN, *Forsch. u. Fortschritte*, **19** (1943) 4.

lattice defects. These distortions change the vibration spectrum of the entire crystal, resulting in an increase of the probability of the dissipation processes.

In the picture of SCHÖN–KLASENS it must be assumed that high activator concentrations cause quencher levels. Such levels may be formed in two ways:

1. formation of activator clusters, i.e. a configuration formed by activator ions occupying neighbouring lattice positions;
2. macroscopic distortion of the crystal by the presence of an amount of activator compound which does not dissolve in the base lattice of the luminophor.

For zinc sulphide — to which this theory is mainly applied — the activator concentrations giving a maximum of fluorescence are so low that the first factor will be negligible, so that only the second one remains. This view is supported by the observation that *ZnS–Cu* or *Ag* containing super-normal quantities of silver or copper are coloured black or brown by Ag_2S and Cu_2S. In other systems, however, the optimum frequently occurs at concentrations which are high enough to find a considerable fraction of the activator ions at neighbouring positions. In Zn_2SiO_4–Mn_2SiO_4 and $(Zn\text{–}Be)_2SiO_4$–Mn_2SiO_4 we have actually found indications of such effects from the emission spectrum: bands of different spectral distribution were found (Sec. 2.3). If we accept the KLASENS theory for the quenching in these systems — and in view of the indications in favour of a bimolecular mechanism this may be permissible (cf. Sec. 2.3 and 3.9) — it may be that certain configurations of manganese ions are responsible for the changed fluorescence, while other ones act as quenchers. The quenching is then caused by the transfer of excitation energy to the quencher. An argument in favour of this view is provided by the quenching effects of iron which occur at concentrations which are so low that a direct disturbance of the manganese centres is improbable (Fig. 62).

In terms of the theory of MOTT–SEITZ, on the other hand, the cause of the quenching must be sought in each centre, itself. Substitution of one or more of the metal ions in the neighbourhood of the activator may have two effects. In the

first place the energy levels of the activator and the probability of the transitions between these levels may be changed. In the second place the vibrational interaction of the central activator ion with the surroundings — and therefore also the probability of the dissipation process — may be changed. Since the quenching is determined by the proportion between the probability of the fluorescence process and of the dissipation process, both factors will affect the quenching point.

Also this model may explain the quenching in zinc silicate and zinc beryllium silicate activated with manganese (Fig. 60). This view is supported by the fact that the quenching is identical for excitation by λ 2537 Å in the Mn_2SiO_4 absorption band and by λ 3650 Å in the characteristic bands of the manganese (Sec. 2.3). The influence of iron can however not be explained. Possibly quenching occurs according to both mechanisms, in the centres according to MOTT, but by iron according to KLASENS.

In *ZnS–MnS* a high manganese concentration creates new centres (Sec. 2.2). A detailed picture of the quenching of the new (red) emission can, however, not be given before the chemical nature of these centres has been ascertained.

3.9 Non-linear luminescence as an indication of a bimolecular mechanism

In Section 3.4 we have seen that non-linear variations of the fluorescence with changing excitation can be explained by assuming a bimolecular luminescence process and a monomolecular dissipation process. It is certainly not the only way in which non-linearity may occur. In cases in which excitation diminishes the active absorption, for instance, such effects are also to be expected.

Yet it seems that the non-linear response, or what amounts to the same, the dependence of the quenching curve on the exciting intensity, adds a new tool to the ones used so far for the detection of bimolecular processes.

In this connection the occurrence of non-linearity with zinc silicates activated with manganese is very remarkable. Since these systems have an exponential decay, it has often

been assumed that the fluorescence process as a whole is monomolecular. This is probably not correct, but excitation with short-wave ultra violet or cathode rays gives rise to free electrons and holes. Other indications in this direction are the occurrence of photo-conductivity as found by HOFSTADTER and HERMAN [1], the occurrence of phosphorescence [2] and the quenching effect of small concentrations of iron- (Sec. 2.3) [3].

3.10 Quenching and Decay

If in a luminophor the circumstances are such that excited electrons are only able to return to the ground state with the emission of radiation, the rate of decay of the luminescence after interruption of the exciting radiation is determined by the slowest link in the chain of processes which connects the exciting absorption with the final emission. If this link is the luminescence transition within an activator, the decay will be exponential (monomolecular process); if it is the recombination of electrons and holes, the decay law is hyperbolic (bimolecular process).

When there are other ways by which the excited electrons may return to the ground state, namely when radiationless transitions are possible, the situation is more complicated. We then have to distinguish between the cases in which the starting point of the new process coincides with that of the decay-determining slowest link in the luminescence chain, and those in which it occurs either earlier or later. In the latter cases only the intensity of the luminescence is diminished, but the decay law remains unaltered. In the first case, however, the rate of decay is increased. This explains the complicated

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[1] R. HOFSTADTER, *Phys. Rev.*, **54** (1938) 864; **56** (1939) 212. R. HOFSTADTER–R. C. HERMAN, ibid., **57** (1940) 936; **59** (1941) 1.

[2] G. R. FONDA, *J. Appl. Phys.*, **10** (1939) 408. H. C. FROELICH–G. R. FONDA, *J. Phys. Chem.*, **46** (1942) 878. H. W. LEVERENZ, *R.C.A. Review*, **7** (1946) 199.

[3] E. G. RAMBERG and G. A. MORTON, *Phys. Rev.*, **55** (1939) 409, come to the same conclusion by measurements of the saturation of fluorescence at high current densities. We are however, not convinced that the theory on which this conclusion is based is correct.

decay phenomena observed by FONDA with Zn_2SiO_4–Mn[1]: at room temperature an exponential decay law is found for products of low manganese contents. Products containing 2% *Mn* or more, i.e., exactly those for which the temperature quenching sets in below room temperature (cf. Fig. 61*a*), show a faster decay which does not follow a simple law. At —180° C, where temperature quenching is eliminated, the decay resumes its simple form and is found to be purely exponential again. Further indications of this effect may be found in the publications by GARLICK and WILKINS[2], GAVIOLA[3], SZYMANOWSKI[4] and PEKERMAN[5]. The decay curves of GARLICK and WILKINS become markedly steeper in the temperature range in which temperature quenching occurs: for ruby above 485° K, $MnCl_2$ above 90° K, *ZnS* and *ZnS–Ag* above 300° K (cf. their figures 4, 6, 13 and 14). GAVIOLA and SZYMANOWSKI, studying the fluorescence of fluoresceïne in solution at high concentrations at which quenching occurs (cf. Section 3.11) observe an increase of the rate of decay.

An example of a system in which the quenching occurs before the system has reached the decay-determining state, is provided by organic europium compounds when the europium emission is excited by absorption in the organic part of the molecule[6].

If we wish to learn something about the probabilities of the emission transitions from the decay, it is necessary to exclude the possibility of such complications and carry out the experiments at a temperature where radiationless transitions do not occur with considerable frequency. On the other hand, analysis of decay curves obtained at temperatures where the emission is partly quenched may show at which point in the reaction chain the quenching occurs and — if the decay is changed — what is the probability of the quenching process.

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[1] G. R. FONDA, *J. Appl. Phys.*, **10** (1939) 408.
K. BIRUS, *Ergebn. Exakt. Naturw.*, **20** (1942) 234.
[2] G. F. J. GARLICK–M. H. F. WILKINS, *Proc. Roy. Soc. London*, **A 184** (1945) 408.
[3] E. GAVIOLA, *Z. f. Phys.*, **42** (1927) 862.
[4] W. SZYMANOWSKI, *Z. f. Phys.*, **95** (1935) 460.
[5] F. M. PEKERMAN, *C.R.* (*Doklady*) *U.R.S.S.*, **52** (1946) 767.
[6] S. J. WEISSMAN, *J. Chem. Phys.*, **10** (1942) 214.

3.11 The temperature quenching in liquid solutions

Although we have restricted ourselves to the consideration of solids and solid solutions, we shall not finish without emphasizing a possible parallel between the temperature quenching in these systems and in liquid solutions. A more or less continuous transition from one state to the other may be effected by passing from true liquid solutions (organic dyes in alcohol, salts of rare earths in water, etc.) via solutions of intermediate viscosity (solutions in glycerol) to solutions of high viscosity (inorganic glasses, supercooled alcohols, boric acid), the latter being adjacent to the crystalline state.

In the simplest cases the temperature quenching is not dependent on the surroundings. Then we have to do with quenching within the molecule (internal quenching) which is supposed to take place along similar lines as the quenching in crystals [1]. The excitation energy is either transformed into vibrational energy of the molecule in its electronic ground state (MOTT–SEITZ), or it is used to bring the molecule in a tautomeric form, the latter state constituting an inactive intermediate state as has also been supposed for the solids (Sec. 3.3).

In other cases an influence of the surroundings has been observed. For such solutions a mechanism closely resembling MOTT's picture for the temperature quenching in solids has been proposed [2]. Here the primary phase of the quenching probably occurs in the configuration formed by the excited centre (ion, atom, complex, molecule, radical) and its nearest neighbours (lattice atoms, solvent molecules). An influence of the rigidity observed with solutions [3] has no parallel in the solid state if we suppose that it operates directly, hindering the migration of atoms or molecules: in solids the

[1] E. TELLER, *J. Phys. Chem.*, **41** (1937) 109.
J. FRANCK–R. LIVINGSTONE, *J. Chem. Phys.*, **9** (1941) 184.
[2] G. N. LEWIS–T. T. MAGEL–D. LIPKIN, *J. Am. Chem. Soc.*, **62** (1940) 2978.
E. J. BOWEN–E. COATES, *Nature*, **157** (1946) 548.
[3] G. N. LEWIS–D. LIPKIN–T. T. MAGEL, *J. Am. Chem. Soc.*, **63** (1941) 3014, note 13*a*.

luminescence is usually quenched at a temperature at which the ionic mobility is still negligible. We believe, however, that the rigidity itself is not the determining factor, but that it is only important as far as it indicates the strength of the prevailing bonding forces. These bonding forces govern the vibrations and are thus directly involved in the quenching.

For the quenching by added ions, or for self quenching [1] the situation is a little different. As soon as an excited molecule finds one of the "quenchers" in the nearest surroundings it may either transfer its excitation energy directly to the quencher without any activation energy [2] or the quencher may influence the temperature dependence, the configuration formed by the excited dye and the surrounding molecules having a higher quenching temperature when these neighbours are exclusively solvent molecules than when a quencher is present among them. In both cases the energy may be used for a chemical process [3] (e.g., $I^- + H^+ \rightarrow I + H$) or it may excite vibrations in the mentioned configuration and is finally lost as heat.

It may well be that the excited molecule is not simply surrounded by the other molecules, but that it reacts with some of them. Then the quenching can be considered as internal quenching of the formed condensation product [4]. According to RABINOWITCH and EPSTEIN selfquenching is thus often due to the formation of a dimer [5]. If the concentration of due molecules and quenchers is low, the chance to

[1] S. I. WAWILOW, *J. Phys., U.S.S.R.*, **7** (1943) 141; *C.R. acad. Sci. U.R.S.S.*, **35** (1942) 100; *J. Exptl. Theoret. Phys., U.S.S.R.*, **13** (1943) 13.
J. Q. UMBERGER–V. K. LA MER, *J. Am. Chem. Soc.*, **67** (1945) 1106.

[2] R. W. STOUGHTON–G. K. ROLLEFSON, *J. Am. Chem. Soc.*, **62** (1940) 2264.

[3] If this phenomenon is approached from the side of the photochemical reaction, the molecules whose fluorescence is quenched are seen as sensitizers. Cf. W. WEST–W. E. MILLER, *J. Chem. Phys.*, **8** (1940) 849; E. V. SHPOLSKY–E. V. GRISHKIN, *J. Phys.* U.S.S.R., **19** (1945) 107.

[4] E. J. BOWEN–A. W. BARNES–P. HOLLIDAY, *Trans. Far. Soc.*, **43** (1947) 27.

[5] E. RABINOWITCH–L. F. EPSTEIN, *J. Chem. Phys.*, **63** (1941) 69.

find a quencher in the nearest surroundings of the dye at a certain moment is extremely small. During the life of the excited state, however, this situation may occur due to diffusion. Therefore the viscosity of the system is directly important [1].

It is only the meaning of this section to indicate the possible existence of a common law, governing the quenching in solids as well as solutions. It seems worth while continuing along this line of thought, obtaining by the comparison new views upon both fields.

3.12 Summary

In this chapter we have seen that luminescence can vary with temperature in various ways. The simplest cases are those in which only one emission band is emitted after excitation in the corresponding absorption band. In more intricate cases the excitation takes place by absorption in a band which does not correspond to the emission; then additional processes must occur intermediately such as the distribution of excitation energy over the various emission mechanisms, transfer of energy from the configuration in which the energy has been primarily absorbed towards that in which the emission finally occurs, and further similar processes which may all depend on the temperature. It depends on the relative rates of the various processes, and on their function in the luminescence process, which of them mainly determines the temperature dependence of the emission.

For the quenching of luminescence in systems in which only one emission band plays a part, two entirely different explanations have been suggested. The explanations of the first type are based on the assumption that there exist no

[1] S. I. Wawilow–J. M. Frank, *Z. Phys.*, **69** (1931) 100.
S. I. Wawilow, *Acta Physicochim., U.S.S.R.*, **7** (1937) 49.
B. Sveshnikow, *Acta Physicochim, U.S.S.R.*, **7** (1937) 755.
H. G. Davis–V. K. La Mer, *J. Chem. Phys.*, **10** (1942) 593.
R. W. Stoughton–G. K. Rollefson, *J. Am. Chem. Soc.*, **61** (1939) 2634.
E. J. Bowen–A. W. Barnes–P. Holliday, *Trans. Far. Soc.*, **43** (1947) 27.

intermediate states of the electronic configuration between the normal excited state and the ground state. In this picture the essential phase of the quenching consists in the transformation of the energy of the electronic excited state into vibrational energy of the system in the electronic ground state. It has been shown that a mechanism suggested by MOTT and SEITZ is acceptable, while the one proposed by MÖGLICH and ROMPE is not.

In the explanations of the second type it is assumed that there exists an intermediate excited state of the electronic configuration between the normal excited state leading to luminescence, and the ground state. This intermediate state may lead to a different luminescence, either in the visible or in the infra red, or the excitation energy may be dissipated. In this explanation the essential phase of the quenching is the transition of the electronic configuration from the normal excited state to the intermediate excited state. This picture must be preferred for systems in which excitation separates electrons from their "holes". A detailed theory for this kind of quenching has been given by KLASENS. Quenching of these two types may also occur in more intricate systems. Table XXVI, *a*, shows a number of cases in which such simple quenching has been observed, together with the theory which is supposed to explain the particular quenching effects most satisfactorily.

While the simple quenching considered above is usually completed within a comparatively narrow temperature range (70–150° C), in some cases a quenching is observed whose quenching range is much wider. Such quenchings may occur as a consequence of different causes. In the table they are summarized under the heading *b*. The first types are those in which the emission consists of a number of bands. It may either be bands originating in similar centres, differing because of a slight difference in the conditions in or round the centres (b_1), or it may be bands originating in quite different centres (b_2). In the latter case difficulties in the identification are only to be expected when the bands happen to have the same or nearly the same spectral distribution. On the other hand a

TABLE XXVI

Type of the variation of the luminescence	Examples		Place where the system has been considered		Theory to be applied
	System	Method of excitation	Chapter	Section	
a. Simple temperature-quenching					
a_1 Fundamental emissions excited in the corresponding absorption bands	ZnS	$\lambda < 3350$ Å	I	12	Mott-Seitz or Klasens
	ZnO	$\lambda < 3800$ Å	I	12	
	CdS	$\lambda < 5200$ Å	I	12	
	$NaCl$	short wave u v	I	12	
a_2 characteristic emissions excited by absorption in the corresponding abs. band	$ZnS-Mn$	4358	VI	2 2; 3.4 3	Mott-Seitz
	tungstates	2537	III	4	,,
	molybdates	2537	III	4	,,
	Ti-luminophors	cath rays	V	5	,,
	$CaO-Sm$	3650	—	—	,,
	$CaS-Sm$	3650	—	—	,,
	$CaWO_4-Sm$	3650	III	8	,,
	$CaWO_4-U$	3650	IV	2	,,
	Ce^{3+}-lum.	3650	—	—	,,
	$Mg_2TiO_4-Mn^{4+}$	3650	II	2.4 4	,,
a_3 transfer emission involving the activator, excited by absorption in the corresponding abs. band	$ZnS-Ag$	3650	VI	2 2; 3 4	Klasens
	$ZnS-Cu$	3650	VI	2 2, 3 4	,,
a_4 emission in centre excited by absorption in base lattice; quenching from the centre	$ZnS-Mn$	$\lambda < 3350$	VI	2 2, 3.7	Klasens(?)
	$ZnS-Ag$	$\lambda < 3350$	VI	2.2; 3.7	Klasens
	$ZnS-Cu$	$\lambda < 3350$	VI	2 2, 3.7	,,
	$ZnO-Zn$	$\lambda < 3800$	—	—	,,
	$CaO-Sm$	cath rays	—	—	Mott-Seitz
	$MgO-Eu$		—	—	
a_5 emission in centre excited by absorption in the abs. band of the activator compound	$ZnS-MnS$	3650	VI	2 2, 3 [illegible]	Klasens
	$CdSiO_3-MnSiO_3$	2537	VI	2 4	Mott-Seitz
	$Cd_2B_2O_5-Mn_2B_2O_5$	2537	VI	2 3	,,
	$Zn_2SiO_4-Mn_2SiO_4$	2537	VI	2 6	,,
b. Abnormally wide quenching ranges					
b_1 characteristic emission of centres existing under slightly different conditions	glasses	3650, 2537	VI	2 12, 3 2	Mott-Seitz
	Mg_2TiO_4-Mn (untempered)	3650	II / VI	2.4 4 / 2 12, 3 2.3	,,
b_2 superposition of bands from different kinds of centres	$CaWO_4-Pb$	2537	III	5	Mott-Seitz
	$MgSnO_3-Ti$	2537	V	5	,,
	Mg_2SnO_4-Ti	2537	V	5	,,
b_3 Excitation in a band not corresponding to the emission (e.g. a band of the matrix lattice); quenching during the transport of energy towards the centres	$ZnS-Cu$(?)	2537	VI	2.2; 3.7	?
	$ZnS-Mn$(?)	2537	VI	2 2; 3 7	?
b_4 Variation in the distribution of excitation energy over the different centres in a two-band system, for instance due to a variation in the relative absorption strength of the bands of the two centres	$ZnS-Cu$	3650	VI	2 2, 3 6	—
	$ZnS-Mn$	3650	VI	2 2; 3.6	—
	$CaS-Cu-Ni$	?	VI	3 6	—

TABLE XXVI (Continued)

Type of the variation of the luminescence	Examples		Place where the system has been considered		Theory to be applied
	System	Method of excitation	Chapter	Section	
c. Increase of luminescence with increase of temperature					
c_1 increase of the high temp. band of a two-band system due to transfer of energy from the low temp. band after independent quenching of the latter	*$CaWO_4$–Sm* *$CdSiO_3$–Mn(?)* *CdI_2–$MnCl_2$*	2537 2537, cath. rays 3650	VI VI VI	3.2.4 2.4 2.5	Mott–Seitz ? ?
c_2 increase of the high temp. band of a two-band system due to temperature dependent transfer of energy from the centres of the low temp. band	*ZnS–Ag–Cu* *ZnS–Zn–Cu* *ZnS–Ag–Mn*	3650 3650 3650	VI VI —	3.2.1 3.2.1 —	Schön–Klasens ,, ,,
c_3 de-blocking of centres which have previously been blocked by electrons, trapped near the centres	?	—	VI	3.2.1	—
c_4 emission in the centres, excited by absorption in a band not corresponding to it (e.g. the absorption band of the base lattice); temperature dependent link in the transport of energy towards the centres	*Li_4SiO_4–Ti* *$MgSiO_3$–Ti* *$SrSiO_3$–Ti* *$Cd_2B_2O_5Mn$*	cathode rays ,, ,, ,, ,, 2537, cath. rays	VI VI VI VI	2.12; 3.7 2.12; 3.7 2.12; 3.7 2.3	— — — ?
c_5 variation of the distribution of excitation energy over different bands (counterpart of b_4)	*ZnS–Cu* *ZnS–Mn* *CaS–Cu–Ni*	3650 3650 ?	VI VI VI	2.2; 3.6 2.2; 3.6 3.6	— — —
d. Quenching by high activator concentrations					
d_1 one activator changes the surroundings for another one, next to which it is placed in the lattice; changed surroundings cause changed interaction with these surroundings	*Zn_2SiO_4–Mn*	2537	VI	3.8	Mott–Seitz
d_2 an activator occupying a position next to another one changes the electric field and thus causes the occurrence of new emission bands with different transition probabilities	*$(ZnBe)_2$–SiO_4–Mn*	2537	VI	3.8	Mott–Seitz
d_3 high activator concentrations cause new intermediate electronic levels, or make the old ones more easily accessible (cf. e_2)	*ZnS–Cu*	3650	VI	3.4.2	Klasens

TABLE XXVI (Continued)

Type of the variation of the luminescence	Examples		Place where the system has been considered		Theory to be applied
	System	Method of excitation	Chapter	Section	
e. Quenching by contaminations					
e_1 reduction of the actively absorbed radiation by a competing absorption (this effect is in first approximation independent of temperature)	$CaWO_4$–Cr	2537	III	7	—
	$CaWO_4$–Fe	2537	III	7	—
	$CaWO_4$–Mn	2537	III	7	—
	Mg_2TiO_4–Mn–Fe	3650	II	2.4.7	—
e_2 decrease of the quenching temperature (mechanism similar to that of d_3?)	ZnS–Cu–Ni	3650	VI	3 8; 3.4.1	Klasens
	ZnS–Ag–Ni	3650	VI	3.8; 3.4 1	,,
	Zn_2SiO_4–Mn–Fe	2537	VI	3 8	Klasens(?)

slow decrease of the intensity may also occur as a consequence of annihilation of the excitation energy during the transport through the lattice (b_3); this effect obviously can only occur in systems in which excitation has taken place in a band not corresponding to the emission, for instance the absorption band of the matrix lattice. Finally for systems in which the exciting radiation is absorbed in the absorption bands of two kinds of centres (either both active, or only one of them active), a change in the relative absorption strength for the particular exciting wave-length may also cause a gradual variation in the intensity of a band; either decrease (b_4) or increase (c_3).

Increase of luminescence with increasing temperature (*c* in Table XXVI) may occur as a consequence of the transfer of energy from another band when the latter band is quenched. In this process it may be that the quenching of the low temperature band occurs anyway, independent of whether the other centres are present or not (c_1) or it may be that the quenching of the low temperature band is dependent on the presence of centres of the other kind (c_2). Further ways in which the luminescence may increase are: an increase in the number of active centres due to the liberation of trapped excited electrons which eliminate the centres at low temperatures (c_3), and a temperature dependent link in the transport mechanism in systems where the excitation energy has to travel towards the centres (c_4).

Quenching at high activator concentrations may be explained in terms of the theory of MOTT or of KLASENS. Both theories probably will find their own field of application. Using the theory of MOTT, the presence of other activator atoms in the neighbourhood of a certain activator atom may change the magnitude and the symmetry of the electric field and may thus cause the occurrence of new emission bands with a different transition probability (d_2), or it may change the surroundings of the activator in mass and in symmetry and thus cause a change in the vibrational interaction (d_1). In the frame-work of the theory of KLASENS the high activator concentration increases the probability of transfer from the normal excited

state to the inactive intermediate excited state of the electronic configuration, either by increasing the number of intermediate electronic levels or by lowering the potential barrier which must be crossed to reach them.

The influence of contaminations on the temperature quenching may be understood in the same way (b_2).

We are aware of the fact that the theories given, and the application of these theories to particular systems, have only a provisional character. Further investigations may show that part of what has been said is not quite correct. We believe, however, that such theories are indespensable for a grouping of the immense amount of scattered observations and that on the other hand these theories, even if incorrect, may be effective in stimulating a systematical research.

APPENDIX

APPLIANCES AND EXPERIMENTAL METHODS

1. EMISSION SPECTRA

For the determination of the spectral distribution of the luminescence, the emission was spectrally decomposed by means of a reflection grating, a spectrograph or a double monochromator and the intensity at each wave-length compared with the intensity of a tungsten ribbon lamp of known colour temperature. In the visible between 4500 and 6500° this could be done visually: an image of the ribbon lamp and the surface of the luminescent powder was formed in one plane. By varying the current flowing through the band lamp, its emission is made equal to that of the luminophor. If we know the relation between current and colour temperature, we obtain the spectral distribution directly in this way. Mostly, however, we used one of the other methods shown in Table XXVII, using either a photographic plate or a vacuum photo-cell connected with an amplifier or a photo-multiplier tube as a recording instrument. Comparison of photographic blackenings was simplified by taking the photographs with the aid of a platinum step-wedge.

For a given colour temperature of the tungsten ribbon lamp the spectral distribution of its emission in the visible was taken from the tables of PLANCK's formula issued by the Bureau of Standards and in the ultra violet from a publication by ORNSTEIN [1].

In order to study the emission at high or low temperatures the powders were pressed close to a metal block by means of a thin quartz plate. The metal block could be cooled by liquid air or could be heated by means of a small furnace attached

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[1] L. S. ORNSTEIN, *Physica,* **3** **(1936)** **561.**

TABLE XXVII

Spectral region	Ultra violet		Visible ($\lambda < 6500$ Å)		Visible $\lambda > 6000$ Å	Visible $6500 > \lambda > 4500$ Å
Apparatus for the spectral decomposition	quartz spectrograph	quartz double monochromator	glass spectrograph	glass double monochromator	reflection grating	glass double monochromator
Recording system	photographic plate	*Cs–Sb* vacuum photocell connected to an amplifier, or a photomultiplier	photographic plate	*K* vacuum photocell connected to an amplifier, or a photomultiplier	photographic plate	eye
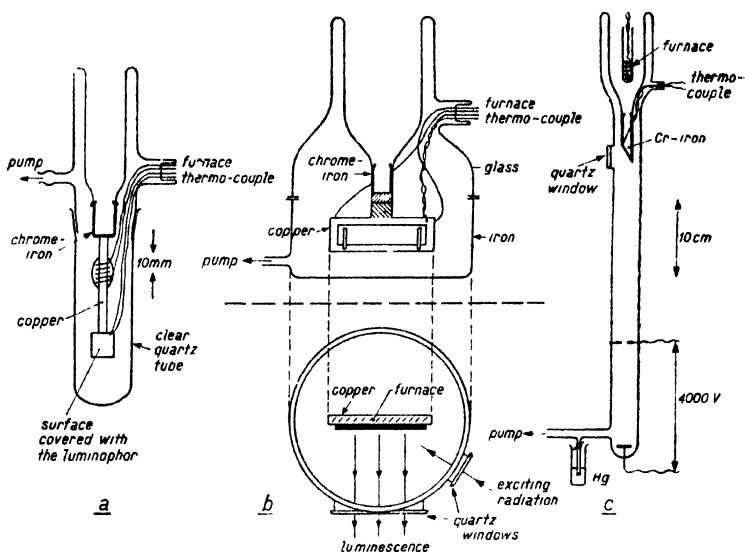
Fig. 74. Apparatus for the measurement of emissions at various temperatures; *a* and *b* for excitation by ultra violet radiation, *c* for excitation by cathode rays.

to it. It was placed in vacuum to prevent condensation. A drawing of the apparatus, showing more of its features, is given in Fig. 74*a*.

2. ABSORPTION AND REFLECTION SPECTRA

For powders the reflection is high for wave-lengths which are faintly absorbed and vice versa. Therefore absorption bands can be determined from the spectral distribution of reflection.

Strong absorption bands cannot be determined accurately. The long wave-length limit of these absorption bands, however, can be found [1].

[1] C. F. Goodeve–J. A. Kitchener, *Trans. Far. Soc.*, **34** (1938) 902.
M. Billy–A. Berton, *C.R. Paris*, **206** (1938) 1631, 1958.

The reflection was measured quantitatively by comparing the reflection of the system under consideration with that of a sample of *MgO*, the reflection of which had been determined in absolute units once and for all with the aid of a thermopile. The comparison took place either photographically with the aid of a spectrograph, or by means of a double monochromator with a vacuum photo-cell connected to an amplifier as a recording instrument (cf. following paragraph). At high or low temperatures, the apparatus described above (Fig. 74*a*) was used.

3. EXCITATION SPECTRA

A rough survey of the spectral region in which photoluminescence is excited, and the luminescence produced in this region, was gained by projecting a spectrally decomposed radiation on to a plate covered with the luminophor. Using alternatively light sources with a line-like and a continuous emission (e.g., mercury and hydrogen discharge tubes) the approximate wave-length limit of the excitation regions can be determined. In order to make observations at various temperatures possible, the plate carrying the luminophor, made of metal, was placed in an evacuated case with quartz windows. It could be either cooled by means of liquid air or heated by means of a small furnace. The apparatus, shown in fig. 74*b*, resembles the one described above (Fig. 74*a*), but is differently dimensioned [1].

Using the classical method of crossed spectra devised by STOKES [2], the method described above was extended for photographic recording by forming an image of the primary spectrum containing the exciting radiation and the luminescence produced by it, on the slit of a spectrograph. The axis of the prisms of the spectral apparatus used are placed perpendicularly, so that the primary spectrum is parallel to the

[1] A similar apparatus is described in the *Handbuch der Experimental-Physik*, **23**, (I), p. 13, taken from R. TOMASCHEK, *Ann. Phys.*, **65** (1921) 200.
[2] STOKES, *Phil. Trans.*, (1852) **463**.

slit of the second spectrograph. In this way the exciting radiation produces a diagonal blackening on a photographic plate placed in this spectrograph, whereas the luminescence is found spectrally decomposed on the same level next to the exciting radiation by which it is produced. This method proved to be especially suitable for the determination of the excitation in systems which show an emission in various emission bands.

A much simpler method, making possible the photographic recording of the excitation spectrum at room temperature uses only one spectrograph [1]. In this method the plate carrying the luminophor, made of a material which is transparent to the luminescence, was fixed closely in front of the photographic plate in the normal cassette, with a thin gelatine filter in between. The filter was chosen to absorb the exciting radiation, but to transmit the luminescence. For luminophors emitting several emission bands simultaneously, the filter was chosen to transmit only one band at a time, thus allowing the determination of the excitation spectrum of the different bands separately.

For one-band systems the plate carrying the luminophor was sometimes combined with the filter by fixing the luminophor on the filter itself. This was suitable for excitation in the far ultra violet where a glass plate shows the required properties [2].

For exact measurements of the efficiency of the luminescence as a function of the wave-length of the exciting radiation, the exciting radiation was spectrally decomposed by means of a quartz double monochromator. The luminophor was placed in the light path behind this apparatus in the centre of an ULBRICHTS' sphere. For measurements at temperatures below or above room temperature an apparatus like that shown in Fig. 74*a* was introduced into the ULBRICHT sphere; reflection on the walls of the container was accounted for as

[1] F. A. KRÖGER, *Physica*, **6** (1939) 373; *Dissertation*, A'dam **1940**, p. 121.
G. R. FONDA, *J. Phys. Chem.*, **43** (1939) 561.
J. W. MARDEN–N. C. BEESE–G. MEISTER, *Trans. Illum. Eng. Soc.*, **34** (1939) 55.

[2] G. HEYNE–M. PIRANI, *Z. techn. Phys.*, **14** (1933) 31.

well as possible. In the more recent experiments the ULBRICHT sphere was replaced by a large aluminium concave mirror as used in projection television (SCHMIDT system). The radiation was measured with the aid of a vacuum photo-cell of known spectral sensitivity, connected to an amplifier, or with a photo-multiplier tube. By interposing suitable filters we successively measured the reflected part of the exciting radiation together with the luminescence (*a*), and the luminescence separately (*b*), whereas a measurement (*c*) of the reflection of MgO placed at the position formerly occupied by the luminophor gave the total intensity of the exciting radiation. When the reflection of the MgO is f_{exc}, the sensitivity of the photo-cell for the exciting radiation S_{exc} and for the luminescence S_{lum} [1], the net energy efficiency of the luminescence is:

$$\eta_{e,n} = \frac{b}{\frac{c}{f_{exc}} - (a - b)} \cdot \frac{S_{lum}}{S_{exc}}$$

and the gross intensity:

$$\eta_{e,g} = f_{exc} \cdot \frac{b}{c} \cdot \frac{S_{lum}}{S_{exc}}$$

The corresponding quantum efficiencies were obtained from these energy efficiencies by multiplication with the quotient of the frequencies of the exciting radiation and the luminescence: [1]

$$\eta_q = \eta_e \cdot \frac{\nu_{exc}}{\nu_{lum}}$$

The reflection of the exciting radiation is also obtained:

$$r = f_{exc} \frac{(a - b)}{c}$$

[1] When the luminescence is in a broad band with a spectral distribution $E_\nu d\nu$, we used the average sensitivity

$$S_{lum} = \frac{\int E_\nu S_\nu d\nu}{\int E_\nu d\nu} \quad \text{and the average frequency} \quad \bar{\nu} = \frac{\int E_\nu \nu d\nu}{\int E_\nu d\nu}$$

As the sensitivity of the photo-cell is dependent on the wave-length, for the determination of S_{lum} it is necessary to know the spectral distribution of the emission. In simple cases this does not offer serious difficulties. When the spectral distribution of the emission differs in different parts of the excitation spectrum however, we have to determine it for each exciting wave-length, which is rather troublesome. In such cases recording by means of a thermopile, the sensitivity of which is independent of the wave-length (it measures directly energies) is far more practical.

4. THE TEMPERATURE DEPENDENCE OF LUMINESCENCE

The temperature dependence of luminescence excited by ultra violet radiation was measured by a simple method. A thin layer of the luminophor was spread over about 4 cm^2 upon the end of a thick copper rod which could either be heated by means of a small furnace fixed round it, or cooled by liquid air. The temperature was measured by means of a chromel-alumel thermo-couple whose junction was fixed at a point of the surface covered by the luminophor. To prevent the formation of rime at low temperatures, the luminophor was covered by an evacuated quartz cuvette.

Exciting radiation of λ 2537 Å was obtained from a low pressure mercury discharge tube (250 mA) made of quartz, wound up in a spiral to give a radiating surface with a diameter of about 8 cm. The visible part of the radiation was omitted by filtering it through 2 cm of a solution of pure iron-free nickel cobalt sulphate, containing about 12% of weight $NiSO_4$ and 8% of weight $CoSO_4$ [1]. In connection with the low surface brightness of this light source we did not form an image of the tube on the luminophor, but placed it as near as possible to the luminophor. Both filter and tube were cooled by a current of air.

Exciting radiation of λ 3650 Å was obtained from a high pressure mercury discharge tube, surrounded by a bulb of

[1] H. L. J. BÄCKSTROM, *Arkiv. för Kemi, Mineral. Geol.*, 13 A, No 24.

WOOD glass (black NiO glass). An image of this light source was formed on the luminophor by means of a lens.

The intensity of the λ 3650 Å radiation was controlled directly with the aid of a selenium blocking layer photo-cell connected to a milli-ampere meter. As these cells are normally not sensitive for λ 2537, in order to control this radiation the ultra violet was transformed into visible light by means of a screen covered with $MgWO_4$, which light could be measured with the photo-cell. The intensity of the emission of the luminophors under investigation was separated from the exciting radiation by interposing suitable filters, and was measured with a selenium blocking layer photo-cell connected to a HARTMANN and BRAUN μ-amperemeter.

For excitation by λ 3650 Å it was possible to measure also the reflected part of the exciting radiation, whereas the reflection of MgO, placed at the position of the luminophor made possible the determination of the total amount of ultra violet falling upon the luminophor. Hence in this case the efficiency could be determined, be it rather roughly and not altogether trustworthily. For excitation by λ 2537 Å, however, only the gross intensity was obtained.

In cases where we wanted to measure the temperature dependence of an emission excited by a radiation of a wave-length for which no intense light source was available (e.g., λ 3130 Å), we used the apparatus shown in Fig. 74*a* and carried out the measurement either photographically or with the aid of the double monochromator and vacuum photocell or photo-multiplier as described in Section 3 [1].

The temperature dependence of luminescence excited by cathode rays was measured with the aid of the apparatus shown in Fig. 74*c*. The tube was run on the pump. A low gas pressure, necessary for a glow discharge, was maintained by means of an adjustable leak. A thin layer of the luminophor was fixed upon the end of a chrome-iron tube which could

[1] The latter method, consisting of the measurement of efficiencies at a number of different temperatures, takes much time but gives accurate results in absolute units and may be useful when well defined data are necessary.

be cooled by liquid air or heated by means of a small furnace inserted in it. The apparatus was not satisfactory, however, the discharge being rather inconstant. In recent experiments it has successfully been replaced by a fully evacuated tube with an uncoated glowing tungsten wire as a source of electrons.

TABLE III

Numbers indicate the references underneath each table

LST = LENARD, SCHMIDT, TOMASCHEK, *Handbuch der Exp. Phys.*, XXIII/I (1928).

s = strong, *m* = medium, *f* = faint

1. Ag

Substance	Colour of the luminescence	References
$AgBr$	blue-violet	23
Ag-borate	white	4
$AgCl$	green	23
AgI	bl. violet; green (—180°)	23; 9
Ag-phosphate	white	4
$AlBO_3$	*f.* blue+yellow	4
Al_2O_3	red+blue	12
$AlPO_4$	*m.* blue+yellow	4
$BaCO_3$–$NaCl$	?	21
$Ba_2(PO_4)_3$	*f.* white-blue	4
Be-phosphate	*m.* yellowish white	4
$CaBr_2$	green or blue	3
Ca-borate	*f.* white-blue	4
Ca-phosphate	*m.* yellowish white	4
CaO	(u.v.)	16
CaS	(u.v.)	10, 15, LST 339
Cd-borate	*s.* yellow	4
Cd-phosphate	*f.* white-blue	4
KBr	(u.v.)	19
KCl	white (at. *Ag*); (u.v.)	22; 11, 19
KI	(u.v.)	19
$LaPO_4$	*f.* blue	4
MgS	blue	14
Mg-phosphate	*f.* white-blue	4
Mg_2SiO_4	violet ?	7
$NaBr$	(u.v.)	11, 19
$NaCl$	white (at. *Ag*); (u.v.)	22; 11, 19
NaI	(u.v.)	19
Na–Ca silicate-glass	yellow (at. *Ag*)	1, 22, 24
$RbCl$	yellow; (u.v.)	3; 11
Sr-borate	*f.* white-blue	4
Sr-phosphate	*f.* white-blue	4
$SrSiO_3$	violet	7
SrS	orange+violet; (u.v.)	LST 369; 10, 15
$SrZrO_3$	yellow	25
Zn-borate	*s.* yellowish white	4

Substance	Colour of the luminescence	References
Zn_2GeO_4	violet ?	7
Zn-phosphate	*f.* white-blue	4
ZnS–$ZnSe$	(greenish yellow)	8
ZnS	(blue)	2, 6, 13, 18, 26
ZnS–CdS	(blue—red)	2, 5, 6, 13, 17, 20
Zn_2SiO_4	violet ?	7

1. G. FISCHER, Neth. Pat. Spec. 55132; 2. S. T. HENDERSON, *Proc. Roy. Soc. London*, (A) **173** (1939) 323; 3. M. HÜNIGER–J. RUDOLPH, B.P.S. 492.722; D.R.P.A. P 74927/P 79557; 4. M. HÜNIGER–H. PANKE, U.S.A. Pat. Spec. 2.270.124; 5. K. KAMM, *Ann. Phys.*, **30** (1937) 341; 6. W. KUTZNER, *Z. Phys.*, **108** (1937) 551; **117** (1941) 575; 7. H. W. LEVERENZ, U.S. Pat. 2.110.162; 8. H. W. LEVERENZ, *Proc.* I.R.E. **32** (1944) 256; 9. W. MEIDINGER, *Phys. Z.*, **40** (1939) 517; **41** (1940) 277.

10. W. E. PAULI, *Ann. Phys.*, **34** (1911) 739; 11. A. M. POLONSKY, *C. rend. acad. sci. U.R.S.S.*, **31** (1941) 543; 12. A. DE ROHDEN, *Ann. Chim. Phys.*, (9) **3** (1915) 366; 13. S. ROTHSCHILD, *Z. Phys.*, **108** (1937) 24; 14. I. SCHAPER, *Ann. Phys.*, **85** (1928) 942; 15. O. SCHELLENBERG, *Ann. Phys.*, **87** (1928) 677; 16. O. SCHELLENBERG, *Ann. Phys.*, **11** (1931) 94; 17. A. SCHLEEDE–F. KORNER, *Angew. Chem.*, **48** (1935) 277; 18. R. TOMASCHEK, *Ann. Phys.*, **65** (1921) 189; 19. A. S. TOPORETS, *Mém. phys. Kiew*, **8** (1940) 161; ref. *Chem. Abstr.*, **35** (1941) 2418.

20. Y. UEHARA, *J. Chem. Soc. Japan*, **61** (1940) 405; ref. *Chem. Abstr.*, **34** (1940) 5348; 21. L. WESCH, U.S.A. Pat. Spec. 2.292.914; 22. W. A. WEYL, *Sprechsaal*, **70** (1937) 578; *Ind. Eng. Chem.*, **34** (1942) 1035; 23. E. WIEDEMANN–G. C. SCHMIDT, *Wied. Ann.*, **56** (1895) 201; 24. P. GILARD–L. DUBRUL–F. JAMAR–D. CRESPIN, *Verre et silicates Ind.*, **8** [35] (1937) 414; ref. *Ceram. Abstr.*, **17** (1938) 247. 25. H. C. FROELICH, U.S.A. Pat. Applic. Serial nr. 498.731. 26. S. ROTHSCHILD, *Trans. Far. Soc.*, **42** (1946) 635.

2. As

Substance	Colour of the luminescence	References
$AsCl_3$	? (—180°); blue	3; 2
AsI_3	yellowish	2
As_2O_3	green; bluish	4; 2
$As_2(SO_4)_3$	pale blue	2
As_2S_3	purplish	2
glass	reddish white	1

1. G. FISCHER, Neth. Pat. Spec. 55132; 2. J. DE MENT, *Fluorescent Chemicals*, Brooklyn (N.Y.), 1942, p. 162; 3. J. T. RANDALL, *Nature*, **142** (1938) 113; 4. E. WIEDEMANN–G. C. SCHMIDT, *Wied. Ann.*, **56** (1895) 201.

3. Au

Substance	Colour of the luminescence	References
glass	whitish	1
ZnS	(blue)	2
$CdWO_4$	orange	3

1. G. FISCHER, Neth. Pat. Spec. 55132; 2. S. T. HENDERSON, *Proc. Roy. Soc. London* (A), **173** (1939) 323; 3. H. G. JENKINS–J. W. RYDE, Brit. Pat. Spec. 528.873.

4. Bi

Substance	Colour of the luminescence	References
a Al_2O_3	bl. violet + orange	7, 11
Al–Ba–Mg-phosph. glass	bluish white	3
$BaCO_3$	green	LST 423; 11
Ba, Sr, Ca phosph.	red	27
BaS	blue + green + orange	LST 381
$BaSe$	red	LST 416
$BaSO_4$	orange	10
BeS	violet	20
$Bi(CH_3COO)_3$	bluish	12
$BiCl_3$	? (—180°)	12; 16
BiI_3	reddish	12
$Bi(OH)_3$	bluish	12
Bi_2O_3	blue	2, 23
Bi_2S_3	black-violet	12
$CaCO_3$	red	14
Ca-borates	blue	
CaO	blue (+ u.v.)	4, 18, 26, LST 419
$CaWO_4$	yellow	9, 19
CaS	blue (+ u.v.)	1, 15, 17, 22, LST 345
$(Ca, Sr)S$	greenish blue	
$CaSe$	red	LST 410
$CaSiO_3$	blue	3A
$CaSO_4$	red	10, 26
$(Cd, Be)WO_4$	yell. green	5
glass	purple	6
MgS	blue	LST 401
$MgSiO_3$	rose	8
SrO	blue	LST 421
SrS	green-blue	13, 15, 17, LST 375
$SrSe$	green + red	LST 412
$SrSO_4$	orange	10
$SrZrO_3$	yellow	25
Zn_2SiO_4	?	21
ZnS	red	LST 397

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5. C

Substance	Colour of the luminescence	References
BN	blue-green	1, 3, 4, LST 600
SiS_2	yell. green	2

1. E. TIEDE–F. BUECHER, *Ber. d. Chem. Ges.*, **53** (1920) 2206; 2. E. TIEDE–M. THIMANN, *Ber. d. Chem. Ges.*, **59** (1926) 1706; 3. E. TIEDE–H. TOMASCHEK. *Z. anorg. Chem.*, **147** (1925) 111; 4. E. TIEDE–H. TOMASCHEK, *Z. Elektrochem.*, **29** (1923) 303.

6. Cd

Substance	Colour of the luminescence	References
Al–Ba–Mg-phosph. glass	bluish-white	2
$CdBr_2$	green-yellow	3
$CdCl_2$	green-yellow	3
CdI_2	green-yellow	3
$MgSO_4$	yellow	1, 4
$ZnSO_4$	blue	4

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7. Co

Substance	Colour of the luminescence	References
glass	orange; bl. green	1; 2
NaCl	yellow	3
$ZnAl_4O_7$	red	5
Zn-borate (glass)	?	4

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8. Cr

Substance	Colour of the luminescence	References
α Al_2O_3	red	3, 4, 5, 6, 7, 11, 14, 5, 17, 18, 20
Al_2SiO_5	red	2, 4
$(Al,OH,F)_2SiO_4$	red	2
$BeAl_2O_4$	red	2, 3
$Be_3Al_2(SiO_3)_6$	red	2, 19
$Ca_3Al(SiO_4)_3$	red	2
$CdAl_2O_4$	red + blue-green	10
chromates and dichromates	pink, red, crimson	12
Ga_2O_3	red	3, 8
LiF	green	16
$MgAl_2O_4$	red	2, 3, 9
Mg–Be silicate (glass)	red	21
$MgGa_2O_4$	red	3
MgO	red	2, 3
Mg_2TiO_4	red	1, 3
$Na_2Si_2O_5$	violet ?	13
$ZnAl_2O_4$	red	3
$ZnGa_2O_4$	red	3

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9. Cu

Substance	Colour of the luminescence	References
α Al_2O_3	green; blue	LST 425, 28; 2, 42
Al–Ba–Mg-phosph. (glass)	rose-white	3
$BaCO_3$	orange, white-blue	LST 423
BaS	blue, green, red	8, 44, LST 378
$(Ba,Sr)S$	yellow	44

Substance	Colour of the luminescence	References
$BaSe$	yellow + red	LST 415
$CaAl_2O_4$	blue	43
Ca-borate (glass)	blue	6
$CaCO_3$	*f.* red	42
CaI_2	blue	4
CaO	blue-green, (u.v.)	LST 419, 31, 32
$3\ Ca_3(PO_4)_2 \cdot Ca(F, Cl, OH)_2$	blue	14
$Ca(PO_3)_2$	blue	7
CaS	blue, (u.v.)	1, 30, LST 332
$CaSe$	bl. green	LST 410
Ca_2SiO_4	blue	34
CdS	infra red	12
$CuBr$	deep purple	23
$Cu.CH_3COO$	purple	23
Cu_2CO_3	reddish	23
$CuCl_2$	green	23, 25, 42
CuI	violet + red	18, 23, 27, 42
CuI_2	purple	23
$CuNO_3$	violet	23
Cu_2O	green; infra red	23; 35, 48
$Cu(OH)_2$	violet	23
CuS	black-violet	23
KBr	violet	36
KCl	violet	36
K–Ca–Sn silicate glass	blue + red (at. *Cu*)	29
Li_4SiO_4	blue-violet	34
$Mg_3(PO_4)_2$	red	23
MgS	green	LST 401
$MgSiO_3$	green	15, 22
Mg_2SiO_4	green; violet ?	34; 22
$Mg_4Si(W_2O_7)_6$	white-blue	34
$NaBr$	violet	36
$NaCl$	violet; yell. green	16, 36
Na_2S	green	LST 404
Na_2SiO_3	blue	34
$Na_2Si_2O_5$ (glass, cryst.)	u.v. + blue	26
Na-silicate (glass)	?	33
Na–Ca silicate (glass)	green—yell. gold	10, 20
solutions	?	11
$SrCO_3$	blue	42
SrO	green + orange	LST 421
SrS	green (+u.v.)	1, 24, 30, 46, LST 363
$SrSe$	green	LST 412
$SrSiO_3$	violet-blue	22

Substance	Colour of the luminescence	References
$SrZrO_3$	red	45
Zn-borate glass	green	6
Zn_2SiO_4	violet-blue	22
Zn_2GeO_4	violet-blue	22
ZnS	green	9, 12, 13, 17, 19, 37, 38, 39, 40, 42, 47
ZnS–CdS	green—red	12, 13, 17, 19, 41
ZnS–ZnSe	(gr. yellow)	21
ZnS–ZnO	green	5

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10. Fe

Substance	Colour of the luminescence	References
α Al_2O_3	red	6
BeS	blue	5
CaO	(u.v.)	3
CaS	blue-green (+u.v.)	2, 4, LST 330
glass	greenish	1
Na_2S	green+blue	LST 403
SrS	blue (+u.v.)	2, 4, LST 363
ZnS	red	7

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11. Ga

Substance	Colour of the luminescence	References
Al_2O_3	red	1

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12. Hg

Substance	Colour of the luminescence	References
$CdBr_2$	orange	1
CdI_2	orange	1
$HgBr_2$	orange	5
$HgBr$	bluish; orange	3; 5
Hg_2Cl_2	orange	3, 4, 5, 6
Hg_2Cl_2 (vapour)	?	7
$HgCl_2$	blue	3
Hg_2CO_3	lavender	3
HgI_2	red (—180°); yellow	1, 2; 6
Hg_2I_2	red-brown	6
$HgSO_4$	blue; yellow	3; 6

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13. Mn

Substance	Colour of the luminescence	References
AlN	red	74
Al_2O_3	green; red	21, 36, 37, 41; 54, 70, 71, 82
$AgCl$	orange	53, 54
$AgBr$	orange	53, 54
$BaSO_4$	—	53, 82
Be_2SiO_4	pink; orange-red	58; 45
BeO	pink	53
$CaAl_2O_4$	green	45
$Ca_3(AsO_4)_2$	yellow	4
CaB_2O_4	green	28
$Ca_2B_2O_5$	red	28
Ca_2BPO_6	yell. green	28
$CaCl_2$	yellow	83
$CaCO_3$	yellow, red	1, 35, 41, 48, 53, 54, 67, 79, 80
CaF_2	green	79, 80, 83
CaI_2	orange	31
$CaLiPO_4$	orange	28
$CaNaPO_4$	yellow	28
CaO	yellow, red	3, 19, 63
α $Ca_3(PO_4)_2$	yellow	28, 83
β $Ca_3(PO_4)_2$	orange; red	23, 28; 3, 88
$Ca_2P_2O_7$	red	3, 4, 67
$Ca_5OH(PO_4)_3$	green yellow	88
$CaSe$	yellow	4
CaS	yellow, orange	3, 18, 25, 59, 67
$CaSO_4$	green	3, 34, 35, 38, 53, 54, 67, 79, 80, 83, 85
$CaSiO_3$	green, yellow, red	14, 22, 23, 45
β Ca_2SiO_4	yell. green	28
$CaSnO_3$	yellow	28
Ca_2SnO_4	orange	28
$CdAl_2O_4$	orange	45
$Cd_3B_2O_6$	yell. green	64
$Cd_2B_2O_5$	red	13, 54, 64, 66 68
CdB_2O_4	green	64, 66
$Cd_2B_6O_{11}$	green	64
Cd_2BPO_6	orange	28
$CdBr_2$	red	32
$CdCl_2$	red	31, 32, 78
CdI_2	red	31, 32, 54
$CdLiPO_4$	yell. green	28
$CdNaPO_4$	orange	28

Substance	Colour of the luminescence	References
$Cd_3(PO_4)_2$	yellow	28
$Cd_2P_2O_7$	orange	18, 23, 28
$Cd_5Cl(PO_4)_3$	red	54
$CdSiO_3$	orange	18, 23, 45, 53, 54, 68, 76A
$CdSO_4$	yellow	49, 78
CsI	pink	2
Glasses	green—red	15, 42, 46
KBr	orange	2
KCl	orange	2, 24
KI	green, red	2
$LiBr$	red	2
LiF	red	69
LiI	orange	2
Minerals	green—red	8
$MgAl_2O_4$	green; red	40, 86; 7
$MgBr_2$	pink	2
MgB_6O_{10}	orange	18
Mg_2BPO_6	orange	28
$MgCO_3$	red	3, 35
MgF_2	orange	90
Mg_2GeO_4	orange-red	43, 93
MgI_2	red	2
$MgLiPO_4$	red	28
$MgNaPO_4$	orange	28
MgO	green; red	69; 53, 54
$Mg_3(PO_4)_2$	orange	23, 28
$Mg_2P_2O_7$	orange	23, 28
MgS .	red	72
$MgSO_4$	yellow, red	16, 35, 38, 54, 67, 79, 83
$MgSiO_3$	red	23, 45, 54
Mg_2SiO_4	red	23, 45, 58
Mg_2SnO_4	green	73
Mg_2TiO_4	red	73
$Mn_3(AsO_4)_2$	pinkish	47
$MnBr_2$	white; red (—180°)	47, 54
$MnBr_2$.4aq	red (—180°)	54
$MnCl_2$	red (—180°)	31, 54
$MnCl_2$.4aq	red (—180°)	54
$Mn(CH_3COO)_2$	red	47
$Mn(COO)_2$	white	47
MnF_2	red (—180°)	54
MnI_2	yellow	47
$MnSiO_3$	red (—180°)	30
$NaCl$	orange, red	16, 24, 51, 54
Na_2SiO_3	—	61
Na_2SO_4	brown; yellow	81, 84; 83
RbI	pink	2

Substance	Colour of the luminescence	References
SiO_2	red	53, 54
$SrAl_2O_4$	red	89
SrO	green	19, 63
$Sr_3(PO_4)_2$	green	88
SrS	green, yellow	25, 27, 91
$SrSe$	green, yellow	26, 52
$SrSO_4$	red	39, 83
$ThCl_4$	—	53
$TlCl$	red	55
$Yt_2(SO_4)_3$	green, yellow	35
$ZnAl_2O_4$	green	7
ZnB_2O_4	green	5, 6, 13, 54
$Zn_3B_2O_6$	orange	13, 18
Zn_2BPO_6	yell. green	28
Zn_4BPO_8	red	28
$Zn_2SiO_4(\alpha)$	green	9, 18, 23, 30, 44, 54, 60, 62, 65, 76
$Zn_2SiO_4(\beta)$	yellow; red (?)	10, 12, 23, 44, 45, 56, 60
$(Zn, Be)_2SiO_4$	green—red	11, 18, 30, 44, 54, 77, 87
$(Zn, Be)_2$ (Si, Ti, Zr, Th) SiO_4	white (*Ti*-blue?)	44, 45
•$(Zn, Cd)_2SiO_4$	yellow	76
$ZnCl_2$	green	31, 78
ZnF_2	orange-yellow	90, 93, 94
Zn_2GeO_4	yell. green	43, 45, 65
ZnI_2	green	31
$ZnLiPO_4$	yell. green	28
$ZnNaPO_4$	yell. green	28
ZnO	—	53
$Zn_2P_2O_7$	red	43, 54
$Zn_3(PO_4)_2$	yell. green, orange	18, 28
ZnS	yellow	17, 18, 20, 29, 33, 50, 53, 54, 57, 75, 92
$ZnSe$	—	53
$ZnSO_4$	red	35, 38, 67, 78, 81, 83

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14. Mo

Substance	Colour of the luminescence	References
Al_2O_3	blue; white	5; 6
$BaMoO_4$	bl. violet; — (—180°)	4, 7; 9
$CaMoO_4$	yellowish green	4, 7, 8, 9
$Ca(PO_3)_2$	green	1
$CaWO_4$	yellow	3, 12
$CdMoO_4$	yellow	9
glass	red	2
Li_2MoO_4	bl. violet; *f.f.* yellowish (—180°)	4, 7; 9
$Li_2Mo_2O_7$	orange (—180°)	9
$MgMoO_4$	white blue; yellow (—180°)	4, 7; 9
$MgO.2MoO_3$	orange yellow (—180°)	9
$MsthMoO_4$	bl. violet	7
Na_2MoO_4	*f.f.f.* white (—180°)	9
$Na_2Mo_2O_7$	orange (—180°)	9
oxides	?	11
$PbMoO_4$	green (—180°)	9
$SrMoO_4$	bl. violet; yell. green (—180°)	4; 7; 9
$ZnO.(1+x)MoO_3$	yellow	9
Zn_2SiO_4	green	1

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15. Nb

Substance	Colour of the luminescence	References
glass	yell. white	1
oxides	?	2
ZnF_2	greenish blue	3

1. G. FISCHER, Neth. Pat. Spec. 55.132; 2. M. HÜNIGER–J. RUDOLPH–G. ASCHERMANN, U.S.A. Pat. Spec. 2.306.626; 3. F. E. WILLIAMS–H. EYRING, *J. Chem. Phys.*, **15** (1947) 289.

16. Ni

Substance	Colour of the luminescence	References
(Ca, Ba)S	?	5
CaS	deep red+yell. green	LST 331
Glass	reddish	1
NaCl	red; yellow	3, 4; 2
SrS	infra red	LST 363

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17. Pb

Substance	Colour of the luminescence	References
(Alk., earth alkali)-silicates	blue, green	31
AgCl	red	18
$BaSiO_3$	violet; blue, green-blue	29; 32
$Ba_2Si_3O_8$	blue	32
$BaSi_2O_5$	u.v.	33
$Ba_3(SiO_3F)_2$	u.v.	33
BaS	bl.+gr.+orange (+u.v.)	LST 380
(Ba,Sr)S	yellow	27
BaSe	red	LST 415
Ca-borate	blue	8
CaI_2	blue, yellow	9
CaO	bl.+yellow+red (+u.v.)	22, LST 419
CaS	bl.+green+orange (+u.v.)	15, 21, LST 342
(Ca,Zn,Pb)-silicate	yellow	25
CaSe	green	LST 410
$CaSiO_3$	violet	23, 29
Cd-borate	yellow	8
$Cd_3(PO_4)_2$	blue	30
$Cd_5P_3O_{12}F$	blue	30
$CdSiO_3$	violet	29
CdI_3	yellow, red	10, 11, 17
CsBr	green	9
glass	yellow—pink; blue, green	4; 12, 13
KBr	purple	14
MgI_2	yellow	9
MgS	green, yellow	LST 401; 2
$MgWO_4$	(blue-green; WO_4!)	table 30
$(Mg,Cd)WO_4$	(blue-green; WO_4!)	table 30
Pb-borate	blue	8
$PbBr_2$	yellow	13, 20, 26
$Pb(CH_3COO)_2$	bluish	13

Substance	Colour of the luminescence	References
$PbCl_2$	yellowish; white-blue; ?	13, 20; 26; 18
$PbClO_4$	yellowish	13
$PbCO_3$	yellowish	13
PbI_2	green; orange (—180°)	26; 11
$Pb(OH)_2$	bluish	13
$Pb(NO_3)_2$	? (—180°)	18
Pb-phosphate	blue	8
$PbSO_4$	yellowish; blue	13, 20, 25, 19, 26
Pb-solutions	green	5, 6, 16
SrO	blue+green	LST 421
SrS	bl.+gr.+red (+u.v.)	15, 21, LST 373
$SrSe$	blue-green	LST 412
Zn-borate	blue	8
Zn-phosphate	blue	8
ZnS	(blue); green	7; 28
Zn_2SiO_4	blue	1, 24
$ZnWO_4$	(blue-green; WO_4!)	table 30

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18. Pt

Substance	Colour of the luminescence	References
Al_2O_3	yell. green	5
$BaPt(CN)_4.4aq$	green	1, 2, 3, LST 511
$CaPt(CN)_4.4aq$	blue	LST 512
$Cs_2Pt(CN)_4.3aq$	blue	3, LST 512
$CuPt(CN)_4.xaq$	blue (—180°)	LST 512
$Er_2(Pt(CN)_4)_3\ xaq$	orange	LST 512
$K_2Pt(CN)_4.3aq$	blue	LST 512
$Li_2Pt(CN)_4.3aq$	orange	3, LST 512
$LiNH_4Pt(CN)_4$ 3aq	green	LST 512
$MgPt(CN)_4xaq$	orange	LST 512
$(NH_4)_2Pt(CN)_4.$ 3aq	green	LST 512
$Pt(CN)_4^{2-}$ (solution)	green	4
$Rb_2Pt(CN)_4.3aq$	blue	LST 512
$SrPt(CN)_4.4aq$	blue	3, LST 512
$Th(Pt(CN)_4)_2.xaq$	bl. green	LST 512
$Yt_2(Pt(CN)_4)_3\ xaq$	orange	LST 512

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19. Re

Substance	Colour of the luminescence	References
Mg_2GeO_4	?	1
Mg_2SiO_4	?	1
Re_2O_7	pink	2
$SrSiO_3$	?	1
$Zn_2SiO_4(\alpha)$	violet	1
$Zn_2SiO_4(\beta?)$	greenish yellow	1
Zn_2GeO_4	?	1

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20. Rh

Substance	Colour of the luminescence	References
$\alpha\ Al_2O_3$	red	1, 2, 3
$Rh(CNS)_3$	crimson	4
RhF_3	purple	4
RhI_3	reddish	4
$Rh(NO_3)_3$	pink	4
$Rh_4(P_2O_7)_3$	blue	4
Rh-salicilate	purple (= blue+red)	4

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21. Sb

Substance	Colour of the luminescence	References
$(Ba,Sr)S$	yellow	12
BeS	yellowish white	10
B_2O_3	orange	4
CaO	yell. green	3, LST 420
$Ca_2P_2O_7$	blue	13
$(Ca, Sr, Ba)_5P_3O_{12}$ (F, Cl, Br)	white-blue	14
CaS	bl.+green+orange	3, 9, LST 340
$CaSe$	yellow	LST 410
$Cd_5P_3O_{12}Cl$	white-blue	15
glass	purple (= blue+red)	6
MgS	green	1, 9, LST 401
$MgSiO_3$	orange-yellow	5
Phosphate-glass	white	2
$SbCl_3$	orange, ? (—180°)	7, 8
Sb_2O_3	bluish	7
Sb_2S_3	purplish blue	7
SrO	green, yellow	LST 421
SrS	yellow	9, LST 372
$SrSe$	red	LST 412
Zn_2SiO_4	?	11

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22. Si

Substance	Colour of the luminescence	References
AlN	blue	1, 2
$Si_2H_2O.(Si_2OH)R$	orange	LST 553

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23. Sn

Substance	Colour of the luminescence	References
Al-borate	green-blue	5
Al-phosphate	yell. green	5
$(\frac{1}{2}Ba,K)Br$	green	3
$(\frac{1}{2}Ba,K)Cl$	blue	3
$(\frac{1}{2}Ba,K)I$	yellow	3
Ba-phosphate	blue	5
Be-phosphate	green-blue	5
$(\frac{1}{2}Ca,K)Br$	green	3
Ca-borate	blue	5
Ca-phosphate	blue	5
Ca-silicate	blue	1A
CaI_2	green	3
Cd-phosphate	yell. green	5
HPO_3	white	6
$H_2Sn_2O_4$	red + violet	2
KBr	green	4
K-borate	green-blue	5
KCl	bl. green	4, 9
KI	yell. green	3, 4
K-phosphate	yellow	5
La-borate	blue	5
La-phosphate	blue	5
Li-borate	green-blue	5
LiI	green	3, 4
Li-phosphate	green-blue	5
$MgBr_2$	yellow	3
$(\frac{1}{2}Mg,K)Br$	blue	3
MgI_2	yellow	3
$NaBr$	blue	4
Na-borate	green-blue	5
$NaHSnO_2$ solution	violet	2
NaI	green	3, 4
Na-phosphate	yell. green	5
NH_4I	orange	4
Phosphate glass	white	1, 7, 14
$RbBr$	green	4
$RbCl$	green	4
RbI	yell. green	4
SiO_2	blue	6, 8
Sn-borate	blue-green	5
Sn-enamel	brownish	2
$SnCl_2$.aq.	brown; ? (—180°)	2; 11
$SnCl_2$-solution	yellow; green	2; 10
$(SnO_3H_2)_5$	rose	2
SnO_2	white; yell. brown	13; 2
$SnO.H_2O$-glass	brownish	2

Substance	Colour of the luminescence	References
Sn-phosphate	blue-green	5
$SnCl_2$-glass	yell. green	2
$(\frac{1}{2}Sr,K)Br$	green	3
$(\frac{1}{2}Sr,K)Cl$	blue	3
SrI_2	yellow	3
Sr-phosphate	blue	5
Zn-phosphate	green-blue	5
Zn_2SiO_4	?	12

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24. Ta

Substance	Colour of the luminescence	References
Ca-silicate	blue	1
Glass	yell. white	2
Oxides	?	3
Zn_2SiO_4	?	4

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25. Th

Substance	Colour of the luminescence	References
$Ca_3(PO_4)_2$	u.v.+violet	1
Glass	reddish white	2
NaF	yellow	3
ThO_2	blue	1, 4, 5
$Th(SO_4)_2$	blue	5

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26. Ti

Substance	Colour of the luminescence	References
α Al_2O_3	red+blue; violet	4, 5; 2
Benitoite (=$Ba(Ti, Si)O_3$)	blue	8
Si-compounds	blue+yell. green	7
Sn-compounds	blue+yell. green	7
Th-compounds	blue+yell. green	7
Ti-compounds	blue+yell. green	7
TiO_2	blue	3
Zn_2SiO_4	blue	1, 6, 7
Zr-compounds	blue+yell. green	7

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27. Tl

Substance	Colour of the luminescence	References
Al-borate	blue	10
Al_2GeO_5	?	1
Al-phosphate	violet	10
Al_2SiO_5	?	1
$(Ba, Sr, Ca)Al_2O_4$	u.v.	24
Ba-borate	blue	10
$BaSiO_3$	violet, u.v.	15, 24
Ba-phosphate	violet, u.v.	10, 24
$(Ba,Sr)S$	yellow	22
Be-borate	blue	10
Be_2GeO_4	?	1
Be-phosphate	violet, u.v.	10, 24
Be_2SiO_4	?	1
B_2O_3	violet	9
Ca-borate	blue	10
CaF_2	blue, yellow	8
Ca-phosphate	violet ,u.v.	10, 16, 24
$Ca_3(PO_4)_2$	u.v.	23, 24
$Ca_3(PO_4)_2.KCl$	u.v.	24
$CaKPO_4$	u.v.	24
$CaS(Bi)$	violet	3
$Ca\ SiO_3$	violet, u.v.	15, 24
Cd-borate	blue	10
Cd-phosphate	violet; u.v.	10, 24
CsI	yellow	8, 11
Glass	white	7

Substance	Colour of the luminescence	References
K-borate	blue	10
KBr	u.v., blue, green, yellow	2, 8, **13**, **14**, **18**
KCl	u.v., blue, green, yellow	2, 8, **12**, **13**, **14**, **18**, **24**
K-phosphate	violet	10
KI	violet + yellow	2, 10, 11, **14**
La-phosphate	violet	10
Li-borate	blue	10
Li-phosphate	violet	10
Mg-borate	blue	10
Mg_2GeO_4	?	1
Mg-phosphate	violet; u.v.	10, 24
Mg_2SiO_4	?	1
Na-borate	blue	10
NaBr	u.v. + violet + yellow	2, **13**, **14**
NaCl	u.v. + violet + yellow	2, **12**, **13**, **14**
NaF	yellow	8
NaI	yellow	8, **13**
Na-phosphate	violet	10
RbI	yellow; blue	8; 11
Sr-borate	blue	10
Sr-phosphate	violet, u.v.	10, 24
TiO_2	yellow	9
Tl^+ (solution)	violet	4, 5, **13**, **17**, **21**
TlB_r (solution)	blue-green	4, 5, **17**, **21**
$TlCl_x$ (solution)	blue	4, 5, 6, **17**, **21**
Tl-borate	blue-violet	10
TlCl	blue (—180°)	19
Tl_2CO_3	greenish yellow	20
Tl-phosphate	blue-violet	10
Zn-borate	blue	10
Zn-phosphate	violet	10

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28. U

Substance	Colour of the luminescence	References
$Al(AlF_2)SiO_4$	yellow-orange	8, 27
$AlBO_3$	green	20
Al_2O_3	bl. + red	15
Arsenates	yell. green	26
$CaCl_2$	green (—180°)	39
$CaCO_3$	red	45
$CaF_2.CaO$	green	42
CaF_2	green	10, 31, 36, 39
CaO	green	20
Ca-silicate	blue	3A
Ca-vanadate	red	
$CaWO_4$	green + red (—180°)	19, 21, 24
Carbonates	green	26
$CdWO_4$	orange	18, 21, 24
CsF	green	39
Glass	green	5, 6, 30, 34, 38, 44, 47, 49
$K.Al(SO_4)_2$	green	39
KBr	yellow (—180°)	39
KCl	yellow (—180°)	39
K_2CO_3	yellow	39
KF	orange	33, 39
KI	yellow (—180°)	39
KPO_3	bl. green	31
K_2SiF_6	green (—180°)	39
$KThF_5$	green	20
K_2TiF_6	orange (—180°)	39
LiF	green	39
Li_3PO_4	green	39
Li_2WO_4	green, orange	21
$MgNaPO_4$	green	39
MgO	red	20
$MgWO_4$	red (—180°)	21
$MgSiO_3$	green	16
Minerals	green	25, 26, 48
Na_3BO_3	green	39
$Na_2B_4O_7$	bl. green	31
$NaCl$	red, yellow	17
NaF	yellow	31, 33, 39, 42
$Na(NH_4)_2PO_4$	green	39
$NaPO_3$	green	31

Substance	Colour of the luminescence	References
Na_3PO_4	green	39
$Na_2U_2O_7$.6aq.	yellow	20
Na_2WO_4	green, yellow	21
Phosphates	yell. green	26
$PbSO_4$	yellow (—180°)	39
RbF	orange	39
Scapolith	green—orange	9, 11, 14
$SiO_2.x$aq.	green	9, 13, 48
Sodalith	orange	9
$SrCl_2$	green	39
$SrCO_3$	yellow	45
$SrSO_4$	yellow	2, 39
$SrWO_4$	red (—180°)	21, 34
$Sr_2W_2O_5$	green	21
Sulphates	yell. green	26
UO_2^{2+} salts	green	LST 514—553, 1, 3, 4, 12, 13, 23, 28, 30, 32, 37, 41, 44, 45, 46
UO_2^{2+} solutions	green	7
UO_3	yellow (—180°)	20
$Zn(NO_3)_2$	green (—180°)	39
ZnO	yellow (—180°)	20
$Zn_3(PO_4)_2$	green	39
ZnS	yellow	41
Zn_2SiO_4	?	43
$ZnWO_4$	orange (—180°)	21

N.B.: Sodalith = $(NaAlSiO_4)_3.NaCl$
Scapolith = $((NaAlSiO_4)_3.NaCl) \cdot (Ca_4Al_5(AlO)\,(SiO_4)_6)$

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29. V

Substance	Colour of the luminescence	References
Al_2O_3	yellow	5, 8
$Ba_2V_2O_7$	yellow	6
CaS	?	10
$Ca(VO_3)_2$	wine red	7
$Ca_2V_2O_7$	red-brown	6
Glass	greenish brown	3
$LiVO_3$	green	7
MgO	yellow	5
Mg_2SiO_4	yellow	2
$Mg(VO_3)_2$	green (—180°)	7
$Msth(VO_3)_2$	yellow	7
$Sr_2V_2O_7$	yellow	6
Vanadyl-pertellurite	lavender	4
Vanadyl-percyanide	green	4
$V_4(P_2O_7)_5$	deep blue	4
Zn_2SiO_4	blue (?); greenish yellow	1; 11
$Zn_3V_2O_8$	yellow	9

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30. W

Substance	Colour of the luminescence	References
Al_2O_3	violet; orange	11; 2
$BaWO_4$	blue; u.v (—253° C)	21; 14*a*
$Ba_2W_2O_5$	green	14*a*
$CaWO_4$	blue	1, 2, 4, 9, 10, 12, 15, 17, 19, 20, 21, 22, 25, LST 508
$(Ca,Cu)WO_4$	yellow	28
Ca_3WO_6	blue (—180°)	14*a*
$CaWO_4$–$PbWO_4$	blue + green	14*b*, 24
$CdWO_4$	bl. green	10, 13, 14*a*, 15, 16, 18, 21,
Glass	white	6
Li_2WO_4	blue (—180°)	14*a*, 21
$Li_2W_2O_7$	blue (—180°)	14*a*
$(Mg,Cd)WO_4$	bl. green	30
$(Mg,Cd)WO_4$–Pb	blue green	30
α $MgWO_4$	blue (—180°)	14*a*
β $MgWO_4$	bl. green	3, 6, 8, 10, 12, 14*a*, 15, 21, 23
$MgWO_4$–*Pb, Cd, Bi, Th, Ce*	bl. green	29
$MsthWO_4$	bl. violet	21
Na_2WO_4	u.v.? (—253°)	14*a*
$Na_2W_2O_7$	green	14*a*
Oxides	?	27
$PbWO_4$	blue (—180°) + green	14*a*
$SrWO_4$	blue	14*a*, 21
Sr_2WO_5	green	14*a*
Sr_3WO_6	green	14*a*
Zn_2SiO_4	?	26
$ZnWO_4$	bl. green	5, 10, 14*a*, 15, 19, 21, 23
$ZnWO_4$–*Pb–Cd, Bi, Th, Ce*	bl. green	29

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31. Zn

Substance	Colour of the luminescence	References
BaSe	red	LST 416
CaO	(u.v.)	10
CaS	bl. green+orange (+u.v.)	LST 339, 11
CaSe	green	LST 410
SrS	yell. green	5, 11, LST 366
SrSe	orange	LST 413
ZnS	(blue)	1, 2, 3, 4, 6, 7, 8, 9, 12, 13, 14

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32. Zr

Substance	Colour of the luminescence	References
Ca-silicate	blue	1
Glass	yellowish	3
SrS	?	10
ZnS	(blue)	6

Substance	Colour of the luminescence	References
Zn_2SiO_4	blue	1A, 5
ZrO_2	bl. green; violet	2, 9; 4
$ZrSiO_4$	blue—yell. green	7
$ZrSO_4$	blue+green-blue	8

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Rare Earths

33. Ce

Substance	Colour of the luminescence	References
AlF_3	u.v.	11
Al_2O_3	yellow—violet	12
$3\ Al_2O_3.2\ SiO_2$	violet	1, 16, 19
$Ba_3(PO_4)_2$	violet	18
Be_2SiO_4	violet	1
$BeSiO_3$	violet	1
CaF_2	u.v.	11
$CaAl_2Si_2O_8$	blue	16
$Ca_2Al_2SiO_7$	blue	16
$Ca(PO_3)_2$	lavendel blue	4, 18
$Ca_2P_2O_7$	violet	18
$Ca_3(PO_4)_2$	violet, u.v.	13, 18, 30
$Ca_3Si_2O_7$	blue	16
Ca_2SiO_4	blue	16
$CaSiO_3$	blue	16
$CeBF_6$	u.v.	11
$Ce_2(CO_3)_3$	u.v.	11
CeO (vapour)	green-blue	7
$CePO_4$	u.v.	11
$Ce_2(SO_4)_3$. 8aq.	u.v.	11
Ce^{3+} solutions	u.v.+violet	5, 11, 15, 21, 22, 23, 24, 25
Glass	blue	2, 3, 10
HPO_3	u.v.	9
KI	blue	8
$LaBO_3$	u.v.	11
$LaCl_3$	u.v.	11
$La_2(CO_3)_3$	u.v.	11
LaF_3	u.v.	11
$La_2Si_2O_7$	violet	17
$La_2(SO_4)_3$ 8aq.	u.v.	11
$MgBr_2$	blue	8

Substance	Colour of the luminescence	References
MgS	green (?)	26
Mg_2SiO_4	violet	1
$MgSiO_3$	violet	1
$Na_2B_4O_7$	white blue	6
Na–Ca-silicate glass	purple	14
Phosphate glass	u.v.	
SiO_2	blue	11, 27
SrF_2	u.v.	11
$SrAl_2SiO_6$	blue	16
$Sr_3(PO_4)_2$	violet	18
$Sr_3Si_2O_7$	blue	16
Sr_2SiO_4	blue	16
$SrSiO_3$	blue	16
SrS	bluish green	29
ThF_4	u.v.	11
ThO_2	orange (Ce^{4+}?)	20
$Th(SO_4)_2$.4aq.	u.v.	11
Zn_2SiO_4	u.v., violet; green (Ce^{4+}?)	16; 4

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34. Dy

Substance	Colour of the luminescence	References
Al_2O_3	bl. green — red	8, 15, LST 492
$CaCO_3$	orange	11
CaF_2	bl. green—red	1, 15, 16, 17, LST 492
$Ca_2P_2O_7$	white (= yellow+blue)	16, 19
CaO	bl. green—red	3, 12, 15, 17, LST 492
$CaSO_4$	bl. green—red	15, LST 493
$CaWO_4$	bl. green—infra red	8, 10
Dy^{3+} (in solids)	orange	1
Dy^{3+}-solution	green	2, 9, 13, 17
$Dy_2(SO_4)_3$.8aq.	bl. green—infra red	4
$Gd_2(SO_4)_3$	yellow	15, LST 493
$La(CH_3COO)_3$.aq.	yell. green	5
$Na_2B_4O_7$	green—infra red	4, 6, 14, 17
$NaCl$	green—infra red	7
NaF	orange	17

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35. Er

Substance	Colour of the luminescence	References
CaF_2	green	1, 6, LST 493
CaO	blue+green	3, 6, LST 493
$Ca(PO_3)_2$	rose	2
$CaSO_4$	blue+green	6, LST 494
$CaWO_4$	green	5
$Na_2B_4O_7$	green	7
$NaCl$	blue+green	4
NaF	green	7

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36. Eu^{3+}

Substance	Colour of the luminescence	References
Al_2O_3	orange	19, 24, 27, LST 482
BaO	red	25
Ba-silicates	orange	16
$BaSO_4$	red	14
BeF_2 (glass)	orange	23
CaF_2	orange	1, 24, 27, LST 483
CaO	orange	4, 19, 24, 25, 27, LST 482
CaS	red	25
Ca-silicates	orange	16
$CaSO_4$	orange	3, 14, 24, LST 484
$CaWO_4$	orange + infra red	19, 21, 24, 25, LST 484
$Eu(BrO_3)_3$.9aq.	orange	14
$Eu_2(C_2O_4)_3$.10aq.	orange	14
$Eu(CH_3COO)_3$4aq.	orange + infra red	14, 23
$EuCl_3$.aq.	orange	5
$Eu_2Mg_3(NO_3)_{12}$ 24aq.	orange	14
$EuPO_4$.4aq.	red	14
Eu^{3+}-solution	orange	2, 20, 22, 23
$Eu_2(SO_4)_3$.8aq.	orange + infra red	5, 22, 23
Gd_2O_3	orange	24, LST 483
$La_2(COO)_3$.aq.	orange + red	6
$La(CH_3COO)_3$aq.	orange + red	6
$MgCl_2$	orange	23
MgO	orange	23, 25
$MgSO_4$	red	14, 23
$Na_2B_4O_7$	orange	5, 7, 9, 27
Na–Ca-borate (glass)	orange	23
Na–Ca-silicate (glass)	orange	23
$NaCl$	orange	10, 15
NaF	red	27
$NaPO_3$	orange	9, 27

Substance	Colour of the luminescence	References
Sr-borate	orange	23
SrO	red	25
$SrSO_4$	red	14
YF_3	orange	1
Eu^{2+}		
$CaCl_2$	blue	18
CaS	yellow (transfer transition)	26
$CaSO_4$	blue	3
$CaSiO_3$	greenish	25
CaF_2	blue	1,11,12,17,25,28
$EuCl_2$	bl. green	5, 12
Fieldspars	blue	8
KBr	blue	12
KCl	blue	12
KI	blue	12
$MgSO_4$	blue	25
$Na_2B_4O_7$	green	5
NaBr	blue	12
NaCl	blue	12
NaI	blue	12
Orthoclase	blue	10
Plagioclase	blue	13
SrF_2	violet	25
SrS	red (transfer transition)	25, 26

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37. Gd

Substance	Colour of the luminescence	References
CaF_2	u.v.	9, LST 484
CaO	u.v.	2, 9, LST 484
Ca-silicate	u.v.	1
$CaWO_4$	?	6
$GdCl_3$.6aq.	u.v.	7, 10
$Gd_2(SO_4)_3$8aq.	u.v.	8, 10
Gd^{3+}-solutions	u.v.	3, 5, 8
$NaCl$	u.v.	4
Zn_2SiO_4	u.v.	1A

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38. Nd

Substance	Colour of the luminescence	References
Al_2O_3	blue+green	5, 10, LST 468
CaO	green+infra red	1, 5, 8, 9, 10, LST 468
CaS	green	8, LST 468
$CaSiO_3$	violet	13
$CaSO_4$	green+infra red	9, 10, LST 468
$CaWO_4$	blue+green+infra red	5, 6
Glass	green—infra red	2, 4, 9, 12
$NaCl$	blue+green+infra red	3
NaF	blue+green+infra red	14
Nd^{3+}-solutions	green—infra red	7
SrS	green	8, LST 468
Zn–Li-silicate	green	11

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39. Pr

Substance	Colour of the luminescence	References
Al_2O_3	green+red	2, 14, LST 463
BaS	green+red	2
CaF_2	green+red	2, 14, 16
CaO	green+red	1, 2, 3, 7, 8, 12, 14, LST 463
CaS	green+red	2, 12, LST 465
$CaSO_4$	green+red	2, 14, LST 463
$CaWO_4$	green—infra red	8, 10
Glass	bl. green—red	7
K_2SO_4	bl. green—infra red	4, 13
La_2O_3	green	5
$NaCl$	green+red	6
Pr^{3+}-solutions	green+blue+u.v.	9, 11, 17
SrF_2	green+red	2
SrO	green+red	2, 12 LST 465
SrS	green+red	2, 12, LST 465
$SrSO_4$	green+red	2
ThO_2	red	15

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40. Sm

Substance	Colour of the luminescence	References
AlF_3	orange	31
Al_2O_3	orange	15, 21, 31, 36, LST 472
$Al_2(SO_4)_3$	orange	29, 31
$BaCO_3$	orange	40
BaF_2	orange	31, 40
BaO	orange	21, 33, 36, LST 475
BaS	orange	29, 31, LST 478

Substance	Colour of the luminescence	References
$BaSO_4$	orange	29, 31
BeF_2	orange	31
BeO	orange	31, 33, 34, LST 475
$CaAl_2O_4$	orange	14
CaB_2O_4	orange	14
$CaCO_3$	orange	26, 40
CaF_2	orange (3+)	3, 14, 16, 21, 27, 31, 36, 39, 40, 41, LST 471
	red (2+)	19
$CaMoO_4$	orange	14, 24
CaO	orange	2, 7, 13, 14, 21, 31, 33, 36, 40, 41, LST 470
$Ca_3(PO_4)_2$	orange	14
$Ca(PO_3)_2$	rose	6
CaS	orange	22, 28, 29, 31, 32, 35, LST 476
CaS–SrS	orange	30, 34, 35
$CaSO_4$	orange (3+)	14, 29, 30, 31, 36, LTS 471
	red (2+)	5, 36
$CaSiO_3$	orange-red	14
$CaWO_4$	orange + infra red	14, 24, 36, LST 472
$CdSO_4$	orange	29, 31
$CdWO_4$–$BeWO_4$ (Bi)	orange	8
CeO_2	orange	31
Ga_2O_3	orange	21, 36, LST 472
$Gd_2(SO_4)_3$	orange	21, 36, LST 471
GeO_2	orange	31
Glass	orange	37
H_3BO_3	orange	1
KNO_3	orange	31
K_2SO_4	orange	29, 31
$La(CH_3COO)_3$.aq.	yell. green—red	10
$La_2(SO_4)_3$	orange	29
Li_2SO_4	orange	29, 31
Lu_2O_3	orange	31
MgF_2	orange	31
MgO	orange	31, 33, 34, LST 475
MgS	orange	29, 31, LST 478
$MgSO_4$	orange	29, 31
$Na_2B_4O_7$	orange + infra red	9, 11, 12, 31, 41

TABLE III

Substance	Colour of the luminescence	References
$NaCl$	orange	18
NaF	orange	41
$NaPO_3$	orange	41
Na_2SO_4	orange	29, 31
$PbSO_4$	orange	30
Rb_2SO_4	orange	29, 31
ScF_3	orange	31
Sc_2O_3	orange	31
SiO_2	orange	17, 31
$Sm_2(SO_4)_3$.8aq.	orange + infra red	9, 20
Sm^{3+}-solutions	orange	4, 23, 25, 42
$SrCO_3$	orange	40
SrF_2	orange	31, 40
SrO	orange	21, 31, 33, 36, LST 475
SrS	orange	28, 29, 31, 32, 35, LST 477
$SrSO_4$	orange	29, 30, 31
ThO_2	orange	31, 38
TiO_2	orange	31
Y_2O_3	orange	31
$ZnSO_4$	orange	29, 31
ZrO_2	orange	31

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41. Tb

Substance	Colour of the luminescence	References
Al_2O_3	u.v —red	13, 18, LST 486
CaF_2	green + red	1, 18, 20, 21, LST 487
CaO	bl. green—red	3, 16, 18, 21, LST 484
CaS	blue + green	16, LST 490
$CaSO_4$	u.v.--red	18, LST 488
$CaWO_4$	u.v.—red	15, 18, LST 488
$Gd_2(SO_4)_3$	u.v.—red	18, LST 488
Gd_2O_3	blue—red	13, 18, LST 487
$La(CH_3COO)$aq.	green + red	7
$Na_2B_4O_7$	bl. green—infra red	6, 8, 10, 21
$NaCl$	?	12
$NaPO_3$	yell. green	10
SrO	blue—red	16, LST 490
SrS	blue	16, LST 490
Tb^{3+}-salts (solid)	bl. gr.—infra red	6, 17
Tb^{3+}-solutions	bl. green—red	2, 4, 5, 11, 14
ThO_2	green	19

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42. Tu

Substance	Colour of the luminescence	References
CaO	u.v.—infra red (3+)	2, 5
$CaSO_4$	red (2+) (—180°)	4
K_2SO_4	blue—infra red (3+)	2
$Na_2B_4O_7$	blue (3+)	1, 3, 5
NaF	red	5
$NaPO_3$	blue (3+)	3
Tu^{3+}-salts (solid)	blue (3+)	3

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43. Yb

Substance	Colour of the luminescence	References
CaF_2	yellowish green (2+)	2, 5, 6, 8
$CaSO_4$	yell. green (—180°) (2+)	9
$CaWO_4$	infra red	7
Glass	orange-red	1
NaCl	?	4
$NaPO_3$	greenish blue	8
SiO_2	yell. green	3

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